

P. 46

## Nonlinear Optical Properties of Rigid-Rod Polymers

Prepared by:

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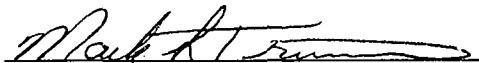
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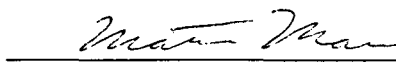
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# NONLINEAR OPTICAL PROPERTIES OF RIGID-ROD POLYMERS

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## Project Summary

**Purpose of the Research.** The purpose of this research project was to integrate enhanced third order nonlinear optical (NLO) properties, especially high  $\chi^{(3)}$  ( $> 10^{-8}$  esu), into Maxdem's novel conjugated rigid-rod polymers while retaining their desirable processing, mechanical, and thermal properties.

**Description of the Research.** This work primarily involved synthetic approaches to optimized materials. Maxdem has, therefore, prepared several modifications of our rigid-rod polymers and has fabricated samples suitable for NLO characterization by JPL. Maxdem has concentrated on preparing the derivatives and measuring chemical, physical, and mechanical properties to help evaluate their potential applicability to optical and electro-optical devices.

**Results of the Research.** Maxdem is developing two families of novel rigid-rod polymers demonstrating good processability (good solubility and moldability) and unique combinations of physical, mechanical, electrical, and optical properties. For instance, members of both families of rigid-rod polymers exhibit excellent mechanical strength and stiffness, good thermal and thermooxidative stability, low thermal expansion, low dielectric constants and loss factors, good optical transparency in the visible spectrum, and moderate values of  $\chi^{(3)}$ . We have also shown that certain of our rigid-rod polymers can be readily blended with significant amounts of other molecules that demonstrate high second order NLO susceptibilities ( $\chi^{(2)}$ ).

**Potential Commercial Applications of the Research.** In light of this work, and the work of others, practical *third order* NLO applications of organic and polymeric materials are still far from realization and will not be realized without considerably more fundamental scientific understanding (e.g. structure-property relationships) of the physical processes involved. In contrast, *second order* NLO technology has developed more rapidly and practical devices may be realized much sooner. The structures of certain of Maxdem's rigid-rod polymers suggest possible second order applications. Others of our rigid-rod polymers may be ideally suited to be utilized as high performance host matrices which contain high concentrations of guest molecules which possess high  $\chi^{(2)}$ 's, but which themselves lack desirable mechanical properties (which is commonly the case). Lastly, several of Maxdem's rigid-rod polymers have properties which make them potentially suitable as dielectric materials for microelectronic and, possibly, opto-electronic applications.

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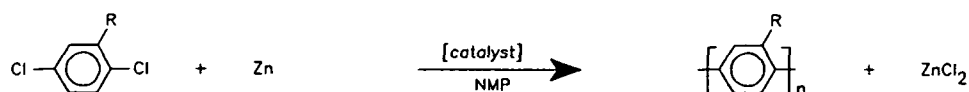
## INTRODUCTION

Recently there has been increasing interest in innovative optical and electrooptical applications in communications, signal processing, computation, and data storage. New materials and concepts are needed for high performance optical switches, limiters and attenuators, spatial light modulators, laser frequency conversion and beam conversion, and sensor protection.<sup>1</sup> An important focus involves devices that utilize the nonlinear behavior of certain materials with light. Practical materials for such applications are required to possess not only high nonlinear activity and ultrafast nonlinear response times but also good processability, environmental stability, good electrical properties, and low optical absorption and scattering. One of the most exciting prospects for meeting all of these criteria are arising in new organics and organic polymers for nonlinear optical (NLO) applications. These organic systems offer a degree of synthetic versatility and processability not possible with the inorganic systems currently used for optical applications.<sup>2,3,4</sup>

Aromatic and heteroaromatic rigid-rod polymers are expected to possess many desirable properties such as good thermal and thermooxidative stability, high mechanical strength and stiffness combined with low weight, and low coefficients of thermal expansion (CTE).<sup>5</sup> Unfortunately, most rigid-rod polymers are extremely difficult to process, often to the extent of intractability. The scarcity of processable rigid-rod polymer systems has greatly curtailed progress in the development of desirable high-performance structural plastics. For instance, molecular composites,<sup>6</sup> blends comprised of a rigid-rod reinforcing polymer (filling the role of the macroscopic fiber in a normal composite) with a flexible polymer (corresponding to the matrix resin), hold great promise as structural materials due to the expected advantages of molecular level reinforcement and the possibility of more practical processability compared with current fiber-containing composites. Unfortunately, even after over a decade of work, molecular composites have not been fully realized because of the difficulty of effectively dispersing current rigid-rod polymers (due to poor processability) and because of phase separation of the rigid and flexible components from the blends (due to incompatibility).

Rigid-rod polymers also hold great promise for electronic and electrooptical applications. A relationship exists between electron delocalization in organic materials and charge conductivity and optical nonlinear susceptibilities;<sup>7</sup> empirical evidence suggests that the delocalization is most effective if it is constrained to one dimension, *i.e.* long conjugated chains. Aromatic and heteroaromatic polymers have extended, conjugated, polarizable backbones and are typically capable of being made conducting and are thus good prospects for certain NLO applications.<sup>8</sup> Indeed, the organic polymers with the highest reported third order susceptibilities ( $\chi^{(3)}$ ) are currently the polydiacetylenes and polyacetylenes ( $\chi^{(3)} \leq 10^{-9}$  esu) and certain aromatic ladder polymers, all of which can also be made highly conducting. Unfortunately, all of these highly conducting (and potentially NLO-active) polymers are extremely difficult to process. Conjugated rigid-rod polymers that could be fabricated into NLO or highly conducting devices or coatings by conventional techniques would have a wide variety of aerospace, defense, and commercial applications.<sup>9,10,11,12</sup>

Maxdem is committed to the technical and commercial development of new types of rigid polymers and applications derived therefrom. Polyparaphenylene is the quintessential aromatic rigid-rod polymer but is not a practical material due to its intractability.<sup>13</sup> Maxdem has invented and is actively developing a new class of processable rigid-rod polyparaphenylenes.<sup>14</sup> These polyparaphenylenes are processable due to the presence of carefully chosen sidechain substituents and are readily prepared by the reductive coupling of substituted dihalo-aromatics (particularly dichloro-aromatics), which is promoted by a transition metal catalyst system which is proprietary to Maxdem Incorporated. We have developed this chemistry into a highly efficient process for polyaromatic synthesis:



Maxdem also possesses the rights to and is pursuing the development of the polyquinoline class of polymers (consisting of both rigid-rod and flexible types of derivatives) which were originally invented and advanced by the late Professor John K. Stille.<sup>15</sup>

Rigid-rod polyparaphenylenes and polyquinolines should have good intrachain delocalization and thus be good candidates for high NLO susceptibilities. Recent calculations suggest that planar (e.g. highly conjugated) polyparaphenylenes should possess some of the highest polarizabilities (related to susceptibility and conductivity) of any organic polymers.<sup>16</sup> Indeed, chemically doped samples of unsubstituted polyparaphenylenes afford highly conducting organic materials ( $\approx 10^2$ - $10^3$  S/cm). Unfortunately, the intractable nature of unsubstituted polyparaphenylenes renders fabrication of devices difficult and also leads to irreproducible behavior. Much effort has been focused on other materials which are less inherently conducting or NLO-active but are more amenable to processing. Unfortunately, these materials generally lack the combination of processability, thermal stability, mechanical integrity, conductivity and/or susceptibility necessary for high performance devices.

The results of Phase I studies by Maxdem of the nonlinear optical properties of first generation proprietary rigid-rod polymers had demonstrated that optical quality films of polyquinolines and processable polyparaphenylenes could be prepared and that they exhibited moderate nonlinear optical behavior ( $\chi^{(3)} \approx 10^{-12}$ - $10^{-11}$  esu).<sup>17</sup> In addition, these high performance polymers were unique in that they could be processed by standard spin-coating techniques. A major focus of the proposed Phase II work involved the further optimization of the inherent nonlinear optical properties of these polymers to obtain much higher third order susceptibilities (e.g.  $\chi^{(3)} \approx 10^{-10}$ - $10^{-8}$  esu) while still maintaining their desirable processing and mechanical properties. It has been estimated that for efficient, low-power switching devices,  $\chi^{(3)}$ 's on the order of  $10^{-9}$ - $10^{-7}$  esu, along with a low loss coefficient of  $< 1 \text{ cm}^{-1}$  and ultrafast response in the picosecond range, would be desirable.<sup>18</sup> It was anticipated that such a material, if demonstrated during Phase II, would be further developed during Phase III efforts.

## PROCEDURES

**General Procedures.** Manipulations involving polymerization catalysts were performed in a Vacuum Atmospheres Corporation Double Inert Atmosphere Chamber under helium. Polymerizations were carried out as described<sup>14,15</sup> in conventional 3-neck glassware under a purified nitrogen gas purge. Viscosities were measured using a Cannon-Fenske opaque (reverse-flow) kinematic viscometer tube suspended in a thermostated bath. Polyparaphenylenes were purified by pouring the reaction mixture into 1 molar hydrochloric acid in ethanol to dissolve the excess zinc metal and to precipitate the polymer. After the gray color had disappeared, the suspension was filtered and the precipitate triturated with acetone and dried to afford fairly pure polymer. Further purification could be effected by redissolving the polymer in NMP, filtering, and precipitating into acetone. After triturating the resulting solid with acetone, it was dried in a vacuum oven (to constant weight) to yield the pure resin.

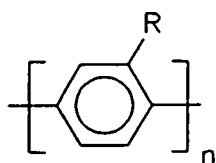
The following instrumentation was utilized by Maxdem for characterization of monomer, polymer, and film samples: Bruker AM-500 NMR spectrometer, Perkin-Elmer 1600 Series FTIR spectrophotometer, Perkin-Elmer 7-Series TGA and DSC, Shimadzu UV-2101 UV-VIS spectrophotometer, Hewlett-Packard 5840A GC with TCD detector, and a Waters GPC-III gradient HPLC/GPC system. Elemental analyses were obtained from Galbraith Laboratories (Knoxville, TN). Electrical properties were measured according to IPC-TM-650 by Trace Laboratories (Linthicum, MD). A film chamber was constructed based on plans provided by the Materials Division at NASA Langley Research Center in Hampton, VA. This relatively simple system is constructed primarily of plexiglass with a system of filters to control dust and humidity. Spin coating was performed using an Integrated Technologies Model 6204 Precision Spin Coater. Maxdem also possesses two Linberg tube furnaces with controllers for pyrolysis and a wide range of equipment designed for electrochemical studies and synthesis.

**Synthesis of 2,5-Dichlorobenzoyl-Containing Compounds.** A wide variety of 2,5-dichlorobenzoyl-containing compounds (e.g. 2,5-dichlorobenzophenones and 2,5-dichlorobenzamides) can be readily prepared from 2,5-dichlorobenzoylchloride. Pure 2,5-dichlorobenzoylchloride is obtained by vacuum distillation of the mixture obtained from the reaction of commercially available 2,5-dichlorobenzoic acid with a slight excess of thionyl chloride in refluxing toluene. 2,5-dichlorobenzophenones (e.g. 2,5-dichlorobenzophenone, 2,5-dichloro-4'-methylbenzophenone, 2,5-dichloro-4'-methoxybenzophenone, and 2,5-dichloro-4'-phenoxybenzophenone) are prepared by the Friedel-Crafts benzoylations of an excess of benzene or substituted benzenes (e.g. toluene, anisole, or diphenyl ether, respectively) with 2,5-dichlorobenzoylchloride at 0-5 °C using 2-3 mole equivalents of aluminum chloride as a catalyst. The solid products obtained upon quenching with water are purified by recrystallization from toluene/hexanes. 2,5-dichlorobenzoylmorpholine and 2,5-dichlorobenzoylpiperidine are prepared in high yields from the reaction of 2,5-dichloro-benzoylchloride and either morpholine or piperidine, respectively, in toluene with pyridine added to trap the hydrogen chloride that is evolved. After washing away the pyridinium salt and any excess amine, the product is crystallized from the toluene solution.

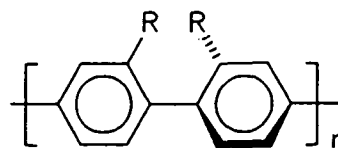
## RESULTS AND DISCUSSION

### Preparation and Chemical Characterization of Rigid-Rod Polymers

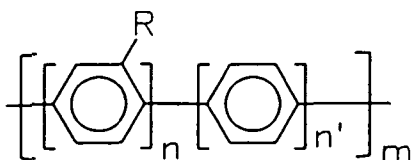
Synthetic efforts have been concentrated on the preparation of several polyparaphenylene derivatives of Types I and II or copolyparaphenylenes of Types III and IV, wherein R can be a variety of groups chosen to provide good solubility, to extend conjugation, or to provide sites for further modification. All of the polyparaphenylenes were prepared by Maxdem's proprietary reductive-coupling polymerization of dihaloaromatic monomers. We have also attempted to prepare ladder type polyquinolines and have performed some modifications of the rigid-rod polyquinoline (ROPOQ) that was studied during Phase I efforts.



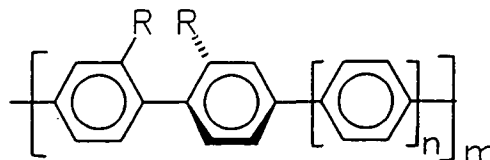
TYPE I



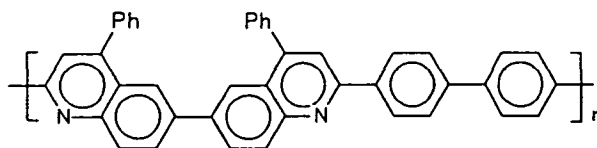
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TYPE III



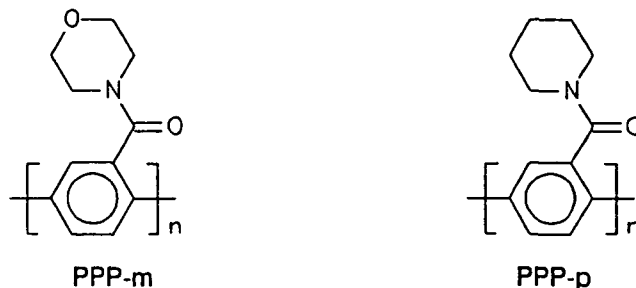
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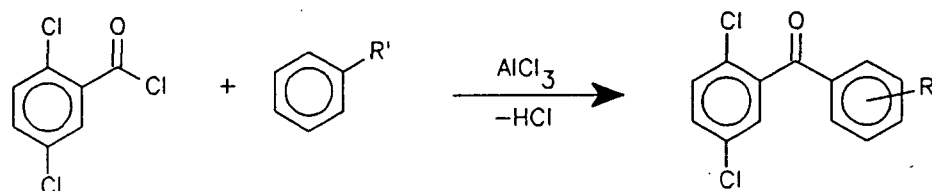
ROPOQ



**Type I Polyparaphenylenes.** During Phase I work to examine the nonlinear optical properties of polyparaphenylenes, efforts were primarily focused on easily prepared amide derivatives (Type I where  $R = -\text{CO-morpholine}$ , PPP-m, or  $-\text{CO-piperidine}$ , PPP-p).<sup>17</sup> We demonstrated that gram-scale quantities of these polymers with moderate molecular weight ( $[\eta] = 1.0\text{-}2.0$  dL/g) could be prepared *via* Maxdem's polymerization procedure and fabricated into good quality films by casting or spin-coating from chloroform and/or NMP solutions. Initial NLO characterization by JPL indicated moderate to good values of  $\chi^{(3)}$  ( $\approx 10^{-12}$  esu).



A large portion of the Phase II effort was based on Maxdem's family of poly(benzoyl-phenylene) derivatives, for which the monomers can be readily prepared in high yield and good purity by the low-temperature ( $0^\circ\text{C}$ ) Friedel-Crafts benzoylation of substituted benzenes ( $R' = \text{H}, \text{CH}_3, \text{OCH}_3, \text{and } \text{OC}_6\text{H}_5$ ):



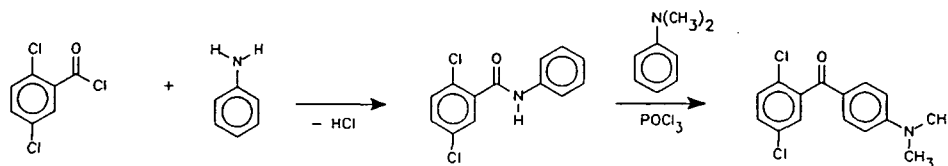
Compared with the amide-type monomers utilized in Phase I studies, the ketone type monomers polymerize much more readily, leading to shorter reaction times (hours rather than days), fewer side-products, and higher molecular weights ( $[\eta] \geq 5.0$  dL/g for PPBP vs.  $\leq 2.0$  dL/g for PPP-m). The ketone derivatives are also easier to purify since they seem to have less affinity to retain solvents or metal salts (which are formed as byproducts in the polymerization reaction). For instance, typical elemental analysis data for samples<sup>19</sup> of PPP-m and PPBP clearly demonstrate the differences:

PPP-m ( $\text{C}_{11}\text{H}_{11}\text{NO}_2$ ) <sub>n</sub>			PPBP ( $\text{C}_{13}\text{H}_8\text{O}$ ) <sub>n</sub>		
	crude	purified		crude	purified
calc	found	found	calc	found	found
C: 69.83	62.11	67.33	C: 86.65	85.02	86.11
H: 5.86	5.86	6.37	H: 4.47	4.10	4.44
N: 7.40	7.00	6.96	N: 0.00	N.A.	N.A.
O: 16.91	20.27	19.14	O: 8.88	N.A.	N.A.
Zn: 0.00	1.50	0.18	Zn: 0.00	<0.015	0.0025
Cl: 0.00	2.48	0.53	Cl: 0.00	N.A.	0.59

Two of the ketone-type monomers ( $R' = H$  and  $R' = OC_6H_5$ ) have been prepared on the multi-kilogram scale by Maxdem for various purposes. During the early part of the Phase II effort, a 100 gram batch of PPBP was prepared (MAX/JPL-II-100) with  $[\eta] = 3.0$  dL/g (measured in 0.05 M lithium bromide in NMP) in order to proceed with film processing, characterization, and chemical modifications. By the end of the Phase II effort, several batches of PPBP and PPPBP had been prepared, at scales up to about 1 kg/batch, with intrinsic viscosities of at least 5.0 dL/g and 3.5 dL/g, respectively.<sup>20</sup> We expect that PPBP with a viscosity of about 6-7 dL/g should have an average chain length of about 100 phenyl rings, although this has not yet been unambiguously determined. These polymers typically demonstrate good solubility (*i.e.* up to about 5% wt/wt at room temperature) in amide solvents (NMP and DMAc), chlorinated solvents ( $CH_2Cl_2$ ,  $CHCl_3$ , dichloroethane, chlorobenzene, *etc.*), anisole, phenyl ether, and *m*-cresol. In other work, we had also demonstrated that this family of polymers can be thermally processed (molded) by conventional techniques (extrusion, compression molding, and even injection molding in certain circumstances).

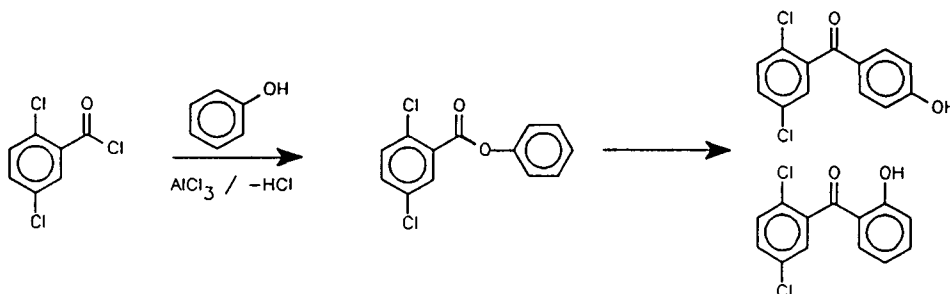
We were also interested in the ketone-type monomers, where  $R' = N(CH_3)_2$  and OH, which we were not able to prepare by the normal route. These groups are electron donating and help to increase the electron density in the conjugated system (which may help to increase the nonlinearity). The resulting derivatives also have somewhat dipolar sidechains (the donating group, hydroxy or amino, is largely para to the withdrawing carbonyl group), which could be used for second order NLO applications, although more elaborate compounds, designed to maximize delocalization, are usually found to give greater effects.<sup>21</sup> If alignment can be induced within these rigid-rod polymers above  $T_g$  (*e.g.* by poling), it is expected that it would be strongly locked in below  $T_g$ , due to the high modulus and viscosity arising from the rigid-rod structure, leading to very good device stability. Finally, these groups are reactive and could be utilized as sites for further modification.

We prepared 2,5-dichloro-4'-(*N,N*-dimethylamino)-benzophenone ( $R' = NMe_2$ ), via a slight modification of the normal procedure, in about 70% yield from the anilide of 2,5-dichlorobenzoic acid:



The corresponding polyparaphenylene was prepared, and a thin film sample (MAX/JPL-II-600) of this polymer was sent to JPL for nonlinear optical (THG) characterization. We also sent some resin (MAX/JPL-II-800) for JPL to cast and then try to pole a thin film (presumably leading to some alignment of the moderately dipolar sidechains) and screen for any resulting second order NLO effects. Unlike most of the other ketone-type polyparaphenylenes that we have prepared, this particular derivative is not particularly soluble in chlorinated solvents like methylene chloride, chloroform, or chlorobenzene but does demonstrate solubility in, and good film casting from, hexafluoroisopropanol (HFIP), formic acid, NMP, and *m*-cresol. We were unable to measure a  $T_g$  for this polymer by DSC analyses.

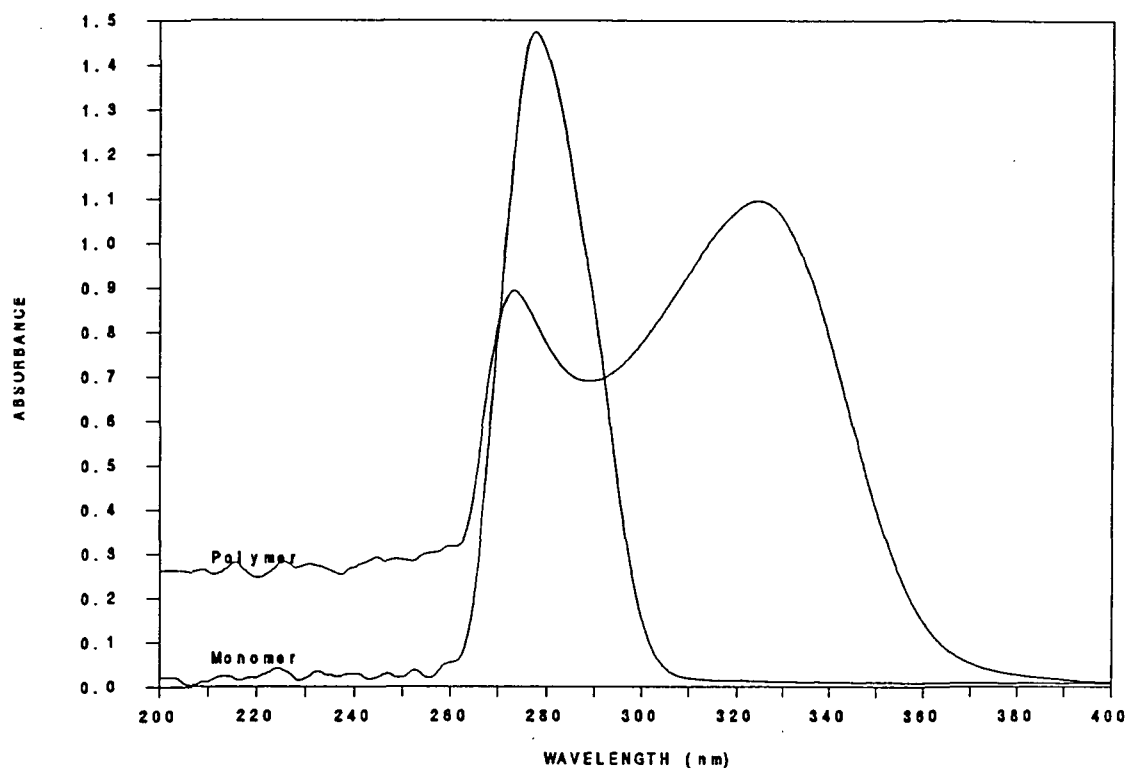
In order to prepare 2,5-dichloro-4'-hydroxybenzophenone, we attempted to perform a Fries rearrangement on the initial ester formed from the reaction of 2,5-dichlorobenzoyl chloride and phenol. As is typical of such rearrangements, a mixture of the 4'-hydroxy and 2'-hydroxy isomers was obtained. Unfortunately, the isomers were difficult to separate and the presence of the 2'-isomer tended to hinder polymerization reactions. Thus after protection of the hydroxy groups by acetylation with acetyl chloride, only low molecular weight polymers were formed. We had previously found that even the presence of 2'-methoxy groups could greatly decrease the efficiency of polymerization reactions, presumably due to the ability of such groups to bind to the metal catalyst during polymerization and prevent further reactions.



We were also interested in examining the nonlinear optical properties of polypara(phenyl-phenylene), PPPP, because of its extended conjugation and expected good thermal and electrical properties. During the course of the Phase II work, another group<sup>22</sup> had reported synthesis of low molecular weight polypara(phenyl-phenylene) by two different routes - from 2,5-dibromobiphenyl *via* the Kumada reaction<sup>23</sup> or by aromatization of a poly(phenyl-1,3-cyclohexadiene) precursor. Some physical properties were also reported but no nonlinear optical characterization was performed. As we expected, the polymer was reported to demonstrate good thermal and thermooxidative stability. Heitz's PPPP also exhibited thermotropic behavior at about  $250^\circ\text{C}$  ( $T_g \approx 195^\circ\text{C}$ ), which suggests that highly ordered films and fibers might be readily prepared. Ordering of rigid polymer chains will greatly increase their mechanical properties. Ordering is also expected to enhance the NLO properties of rigid-chain polymers in certain directions.<sup>24</sup>

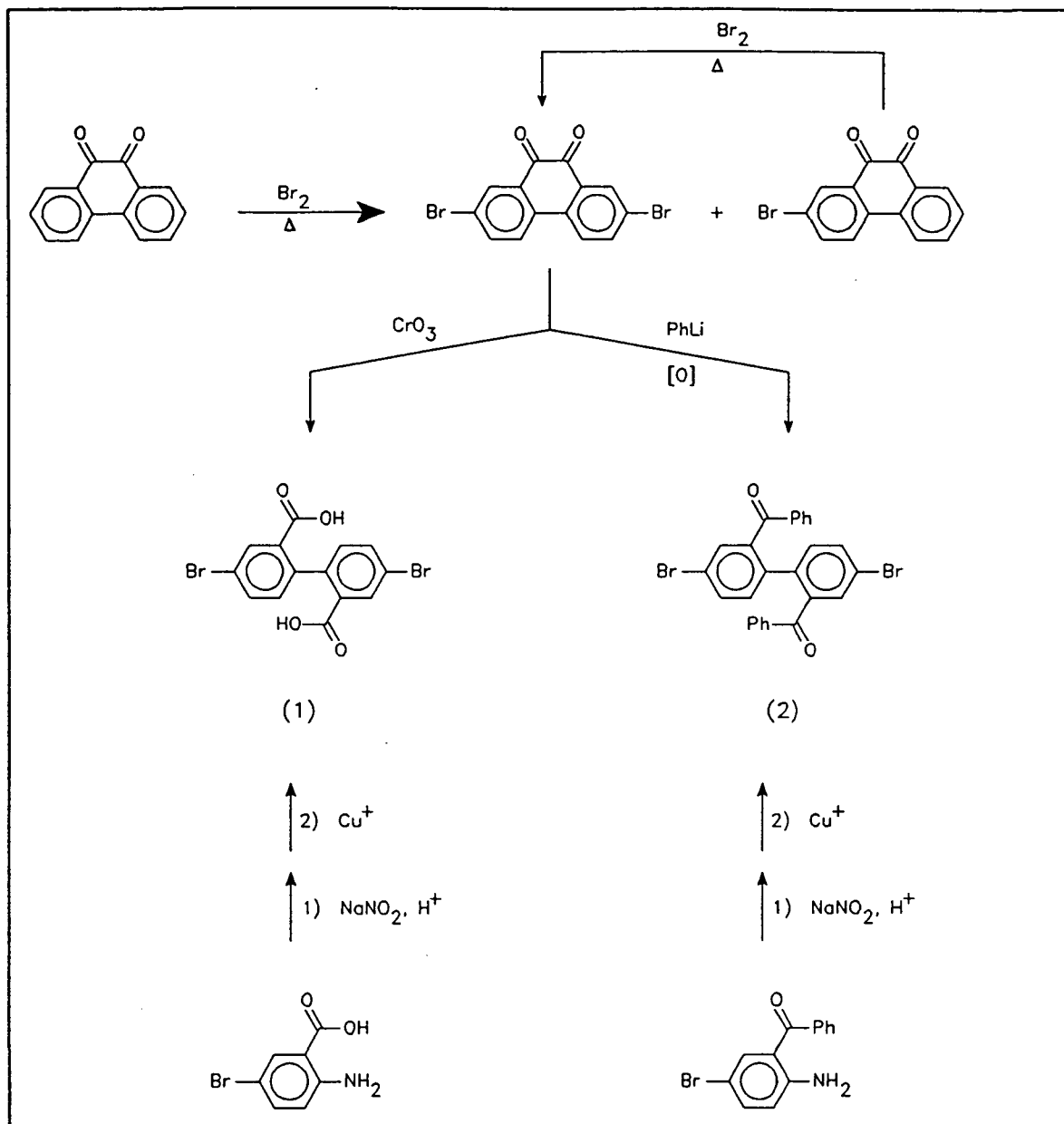
We proceeded to synthesize 2,5-dichlorobiphenyl, the monomer to prepare phenylated polyphenylene *via* our polymerization process, by the phenylation of dichlorobenzene with dibenzoylperoxide.<sup>25</sup> We were able to utilize our polymerization process to prepare an initial sample of poly(phenyl-1,4-phenylene). The molecular weight that was attained was fairly low, probably due to the slow polymerization of the monomer and possibly to some impurities that were difficult to remove from the monomer. The absorption spectra of the monomer and polymer are compared in Figure 1 and clearly demonstrates that polymer has indeed been formed as evidenced by the increase conjugation (absorption band at 330 nm).

**Figure 1.** Absorption spectra of 2,5-dichlorobiphenyl and poly(phenyl-1,4-phenylene).



**Type II Polyparaphenylenes.** We examined two different routes into dihalobiphenyl monomers suitable for the development of the type II polymers described above. One approach involved direct bromination of readily available starting materials. For instance, procedures have been reported for the direct bromination of phenanthrenequinone<sup>26</sup> which can be readily converted to the diphenic acid (1) or dibenzoyl biphenyl (2) derivative (SCHEME I - top). The second approach involved the coupling of aryl diazonium ions in the presence of copper salts to form biphenyls (SCHEME I - bottom). The success or failure of these types of reactions is very dependent upon the identity of the substituent R and a wide variety of side reactions (halogenation, reduction, and azo formation) can be operative. In general, none of the reactions that we tried were able to produce good yields of the desired dihalobiphenyl monomers in sufficient purity for the nickel catalyzed polymerization that we are utilizing. Significant amounts of products were formed in some cases which could have been isolated by tedious procedures (e.g. column chromatography), however, we resisted such techniques for practical reasons.

SCHEME I



**Type III Copolyparaphenylenes.** Copolymers were prepared consisting of substituted and unsubstituted comonomers in order to try to obtain blocks of unsubstituted phenylene units. Polyparaphenylene copolymers were initially prepared by utilizing mixtures of either 4,4'-dibromobiphenyl (DBP), 1,4-dichlorobenzene (DCB), or 1,4-dibromonaphthalene (DBN) as comonomers with 2,5-dichloro-4'-phenoxybenzophenone (DCPBP). We used DCPBP in hopes of obtaining greater copolymer solubility than might be achieved with shorter sidechains. The resulting copolymers were comprised of substituted and unsubstituted 1,4-phenylene backbone units, ranging from about 33-80% (mole %) substituted units. No attempt was made to

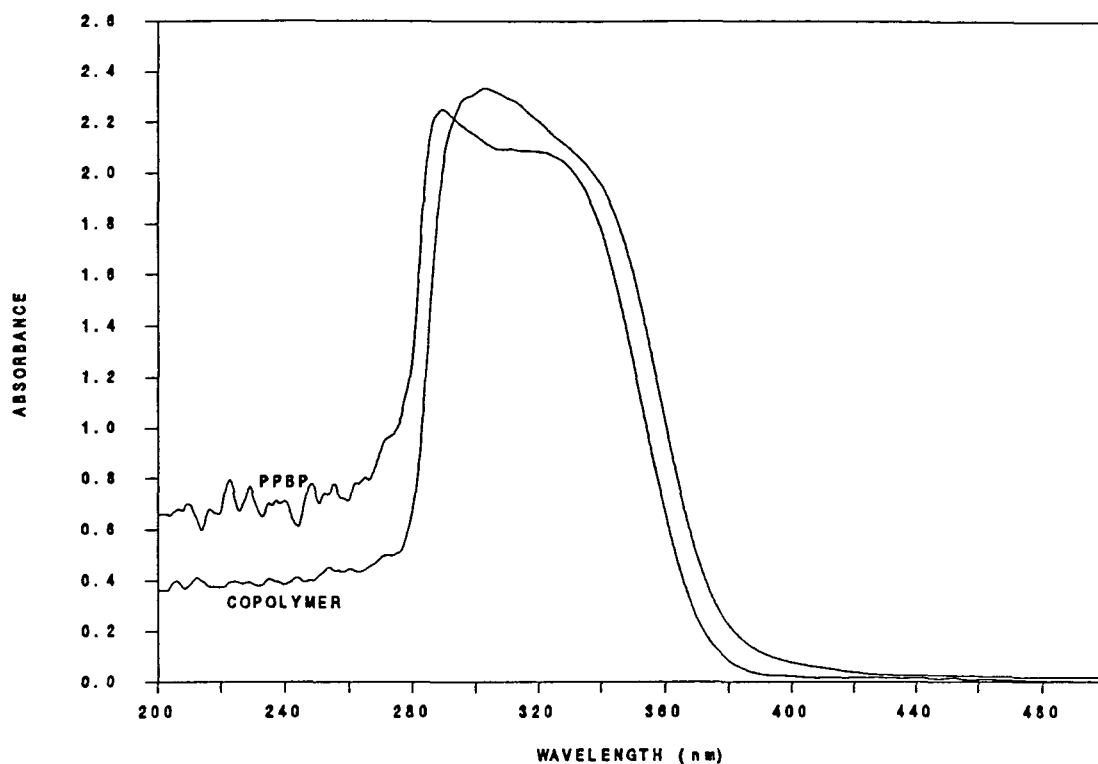
characterize the orientation of the different monomer groups along the polymer chain. A sample of polypara-(4'-phenoxybenzoyl)-phenylene (PPPBP) homopolymer (MAX/JPL-II-400; GPC  $M_n$  = 150,000) was also prepared for comparative purposes. The following copolymer samples were prepared:

SAMPLE	MONOMER COMPOSITION	% SUBST
MAX/JPL-II-410	80/20 DCPBP/DCB	80 %
MAX/JPL-II-420	50/50 DCPBP/DCB	50 %
MAX/JPL-II-430	80/20 DCPBP/DBP	67 %
MAX/JPL-II-440	50/50 DCPBP/DBP	33 %
MAX/JPL-II-450	80/20 DCPBP/DBN	80 %
MAX/JPL-II-460	50/50 DCPBP/DBN	50 %

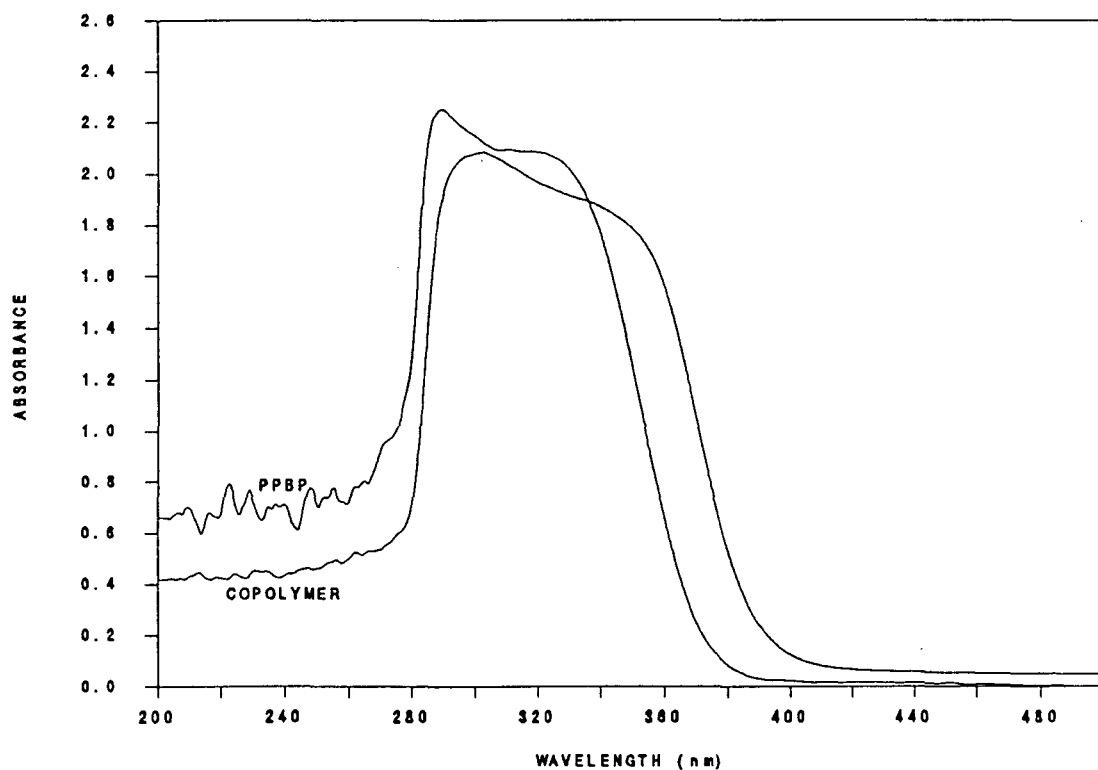
Note that incorporation of dichlorobenzene or dibromobiphenyl as comonomers yields essentially the same type of copolymer, a backbone consisting only of substituted and unsubstituted phenylene units. The use of DBP allows a lower percentage of substituted phenylene units yet leads to a backbone orientation that necessarily consists of adjacent unsubstituted phenylene moieties. It would be extremely interesting to compare the mechanical and nonlinear optical properties of copolymers containing an equal percentage of sidechain but different orientations of the comonomer units (e.g. compare 50/50 DCPBP/DCB and 67/33 DCPBP/DBP). Unfortunately, these copolymers exhibit quite drastic changes in solubility with decreasing extent of substitution. Similar decreases in solubility have been recently noted for some related long chain alkyl substituted polyparaphenylene copolymers.<sup>27</sup> They are also observed to have lower molecular weights (by GPC measurements), possibly due to early precipitation, as the percentage of sidechain decreases. The naphthalene containing copolymers seem to exhibit better solubility but the molecular weights are much lower. We think that naphthyl bromide bonds are readily reduced under our polymerization conditions, leading to chain termination.

SAMPLE	% SUBST	$M_n$ (GPC)	NMP SOL	CHCl <sub>3</sub> SOL
410	80	97,000	SOL	DIFFICULT
420	50	43,000	SLIGHT	INSOL
430	67	78,000	DIFFICULT	INSOL
440	33	-----	INSOL	INSOL
450	80	27,000	SOL	SOL
460	50	15,000	SOL	SOL

**Figure 2.** Absorption spectra of spin-coated films of MAX/JPL-II-410 and PPBP.

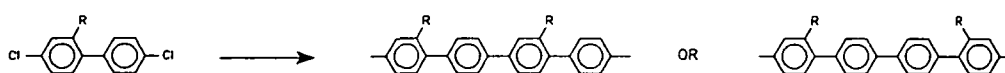


**Figure 3.** Absorption spectra of spin-coated films of MAX/JPL-II-450 and PPBP.

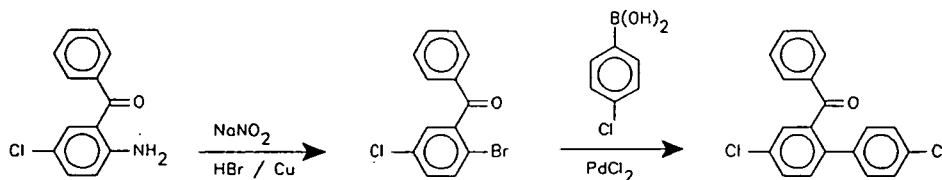


MAX/JPL-II-410 was readily processed from chloroform and/or NMP solutions and free-standing and spin-coated films were obtained. The other copolymers, however, were either too insoluble or of too low molecular weight to give good films by either of these methods. We were able to prepare a thin supported film of MAX/JPL-II-450 by coating a glass slide with a thin solution and allowing the solvent to evaporate. Transparent free-standing films of MAX/JPL-II-400 and MAX/JPL-II-410 from chloroform were sent to JPL for NLO measurements. Comparative UV-Vis spectra of PPBP with MAX/JPL-II-410 (Figure 2) and MAX/JPL-II-450 (Figure 3) are reproduced below. There appears to be a small shift toward longer wavelength for the naphthalene containing copolymers (e.g. MAX/JPL-II-450).

We speculated that the presence of sizeable blocks of unsubstituted poly(para-phenylene) units in the above copolymers might greatly reduce their solubility. We wanted to compare the solubility, as well as the mechanical and nonlinear optical properties, for copolymers containing an equal percentage of sidechain but different orientations of the substituted and unsubstituted comonomer units. In order to prepare a "copolymer" with a more well controlled structure, we proposed an unsymmetrical biphenyl type monomer which will form a 1:1 copolymer with block sizes of only one or two monomer units:

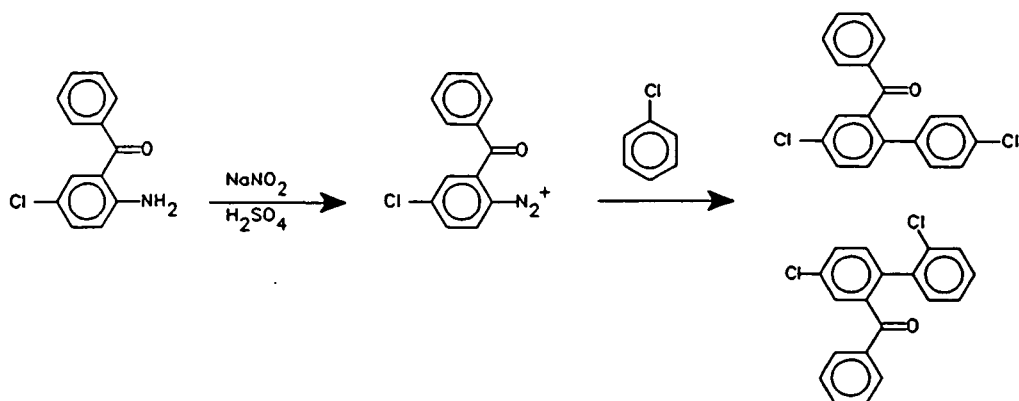


During Phase II, such a polymerization was performed by using the unsymmetrical biphenyl monomer, 2-benzoyl-4,4'-dichlorobiphenyl, prepared by the Suzuki coupling<sup>28</sup> of 2-bromo-5-chlorobenzophenone (prepared from 2-amino-5-chlorobenzophenone) and 4-chlorobenzeneboronic acid:



We had also attempted to prepare the unsymmetrical monomer by the diazotization of the commercially available aminobenzophenone in chlorobenzene, but the poor selectivity of this reaction lead to a mixture of 4,4'- and 4,2'-isomers which were difficult to separate:



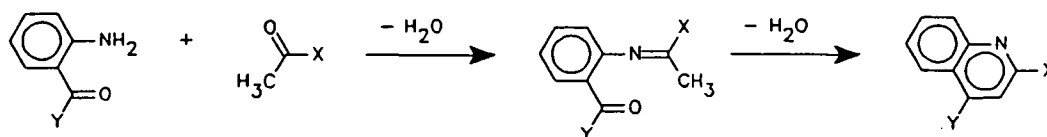


Unfortunately, when 2-benzoyl-4,4'-dichlorobiphenyl was polymerized under Maxdem's conditions, solubility of the resulting polymer did not appear to be greatly improved as some precipitation was observed from the reaction mixture. However, slightly better results were obtained when a mixture of 2,5-dichlorobenzophenone and 2-benzoyl-4,4'-dichlorobiphenyl (10/90 mixture) was copolymerized. Molecular weights were sufficiently low in all cases such that good quality films could not be obtained for optical or mechanical characterization.

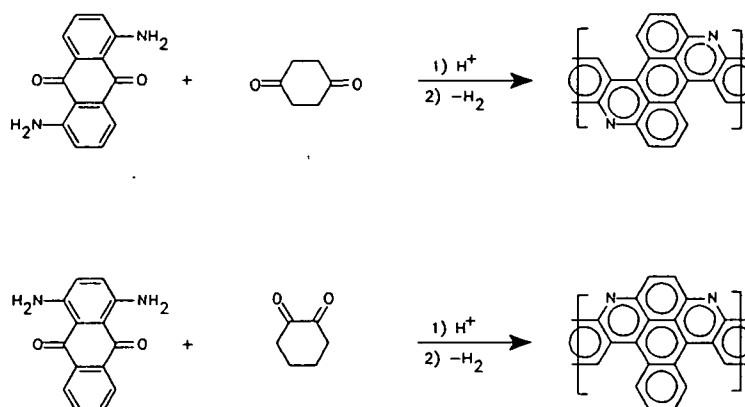
Perhaps more promisingly, we have recently found during other work that the addition of relatively small amounts (10-20%) of 1,3-dichlorobenzene (*m*-DCB) as a comonomer can considerably increase the solubility of substituted polyphenylenes. While technically no longer rigid-rod polymers since the 1,3-phenylene linkages are not linear, these copolymers still maintain many of the desirable properties associated with rigid-rod homopolyparaphenylenes (good optical properties, good mechanical properties, good thermal stability, etc). A solvent cast thin film sample (MAX/JPL-II-700) of a PPBP copolymer comprising about 15% 1,3-phenylene units was sent to JPL for evaluation. We suspected that the addition of some small amount of *m*-DCB (e.g. 10%) would also increase the solubility of copolymers containing unsubstituted phenylene units. During Phase II, some terpolymers, derived from 2,5-dichlorobenzophenone, 1,3-dichlorobenzene, and 1,4-dichlorobenzene were prepared in hope of obtaining soluble copolyphenylenes with substantial numbers of unsubstituted 1,4-phenylene units in the polymer backbone. Indeed, preliminary results indicated that incorporation of about 10% 1,3-phenylene monomers units yielded soluble copolymers containing up to about 40-50% unsubstituted 1,4-phenylene units, the remainder of the units being 1,4-(benzoylphenylene) monomer units.

**Type IV Copolyparaphenylenes.** Due to the lack of success in preparing pure Type II polyparaphenylene monomers which yielded high molecular weight polymers, we did not attempt to prepare any of the Type IV copolyparaphenylenes.

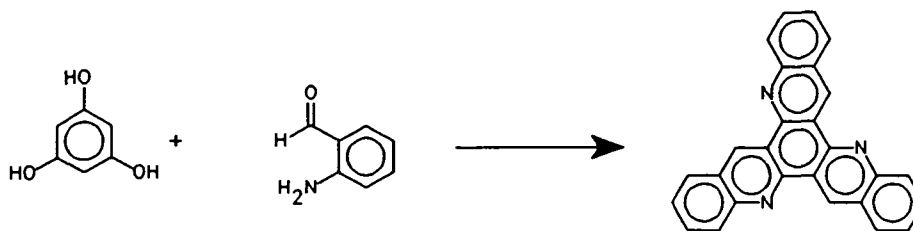
**Ladder Type Polyquinolines.** In general, the Friedländer<sup>29</sup> synthesis of quinolines involves the reaction between 2-amino-arylketones and keto-methylene moieties *via* the intermediate Schiff's base complex as exemplified by:



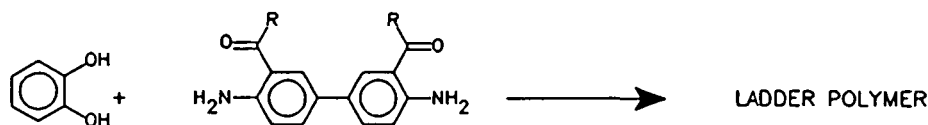
Straightforward attempts were made to prepare novel ladder type polyquinolines from 1,4- and 1,8-diaminoanthraquinones by the Friedländer synthesis. Model reactions of these compounds with acetophenone were performed (150-300°C in polyphosphoric or acetic acid with sulfuric acid or zinc chloride as a catalyst) and afforded a mixture of the Schiff's base complexes along with some cyclized diquinoline. The Schiff's base could be converted to the diquinoline upon heating at very high temperature without solvent. Extension of the procedure to diketone moieties (1,4-cyclohexadiene or diacetylbenzene) for the synthesis of ladder polymers, as shown below, led to high yields of insoluble black materials when carried out with acetic acid, NMP, or m-cresol as solvent and PPA, P<sub>2</sub>O<sub>5</sub>, sulfuric acid, or diphenyl phosphate (DPP) as catalyst. Unfortunately, the polymers are insoluble even in concentrated sulfuric acid and are likely of low molecular weight since they precipitate during the polymerization reaction.



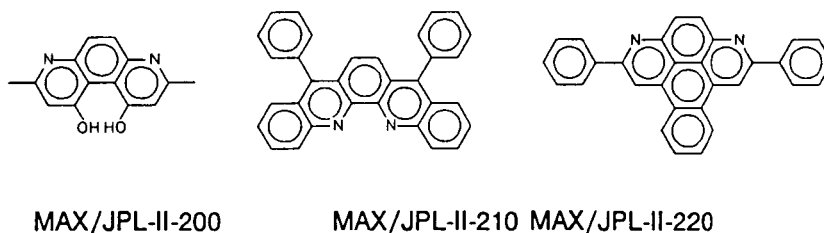
Another approach was inspired by a literature report<sup>30</sup> that phloroglucinol condensed 2-aminobenzaldehyde to form a heterocyclic ring system:



We had hoped that inexpensive catechol might react with suitable bis(aminoketones) to form polyquinoline ladder systems. Unfortunately, the reaction of catechol with 3,3'-bis(benzoyl)-4,4'-benzidine gave only low yields of intractable products under various conditions.



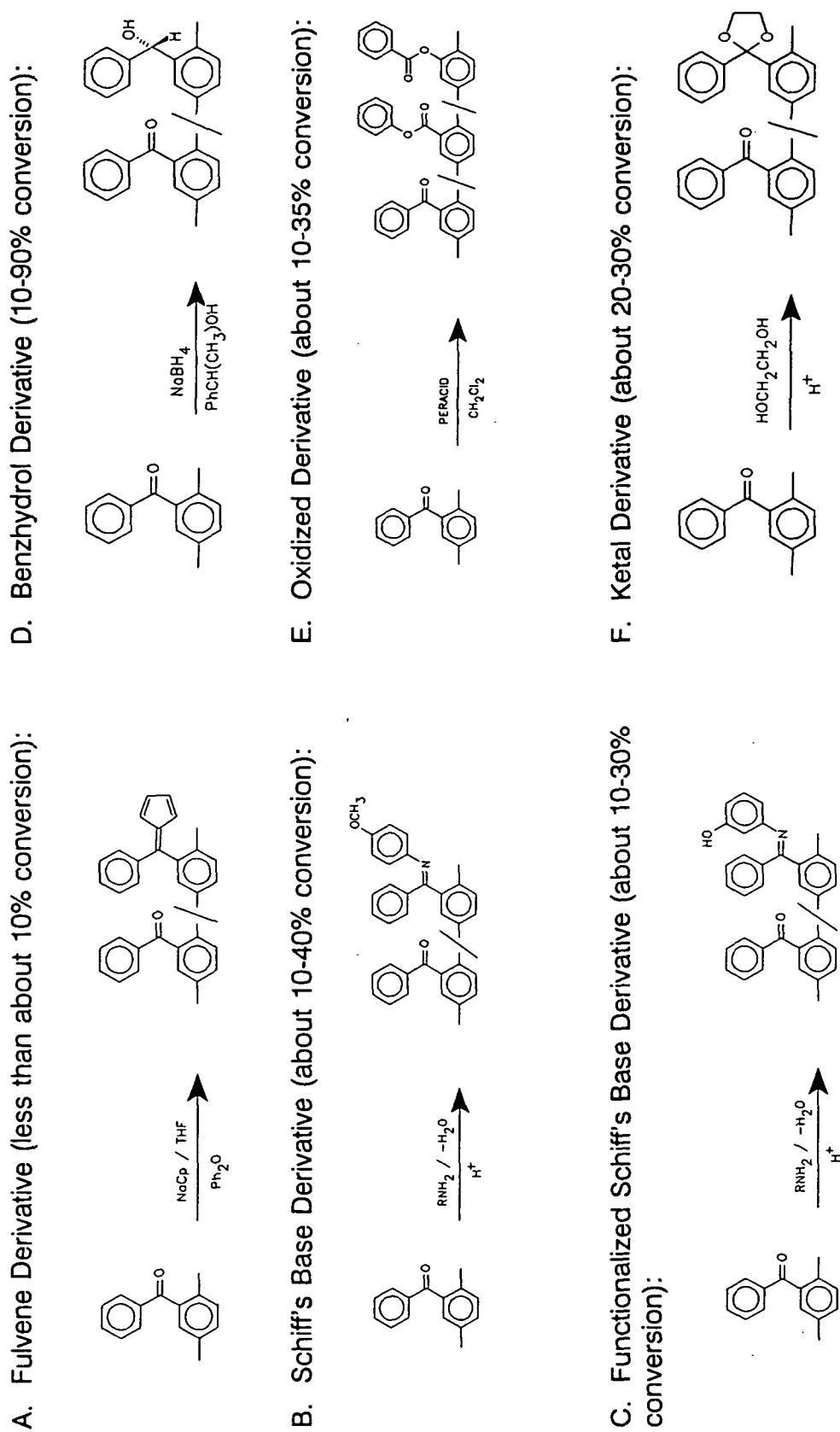
Since our attempted syntheses of ladder polymers generally led to intractable black materials, we isolated some of the polyquinoline fragments obtained from the model reactions and have submitted three samples (solutions) to JPL for screening of their nonlinear optical properties. Promising fragments could be incorporated into other more processable polymer matrices, including polyphenylenes or flexible polyquinolines, in order to make practical nonlinear optical materials.<sup>31</sup> The three-ring polyquinoline ladder fragment, MAX/JPL-II-200, was prepared by the condensation of *para*-phenylenediamine and ethylacetoacetate and demonstrates excellent solubility in ethanol. Two five-ring polyquinoline ladder fragments were also isolated: MAX/JPL-II-210 was prepared from the condensation of 2-aminobenzophenone and catechol, and MAX/JPL-II-220 was prepared from 1,4-diaminoanthraquinone and acetophenone. The five-ring fragments are less tractable than the three-ring species, but 1% solutions can be prepared in NMP. The absorption spectra of these fragments are reproduced in Appendix D - Figure 1.



## Post Polymerization Modifications

In our Phase II proposal, we identified derivatization, or other types of chemical modifications, as an important technique by which to potentially enhance the nonlinear optical properties of our rigid-rod polymers while retaining their other desirable characteristics. During work on various projects, we had demonstrated diverse derivatization chemistry of the carbonyl group in PPBP, which is our most well studied and readily prepared polymer. As summarized in *Scheme II*, we have identified several types of these reactions of possible interest in optoelectronic applications. For example, such reactions could be utilized as methods to chemically append NLO active dyes or other types of dopants onto our polymer backbone, to enhance processability (lower melt viscosity or increase solubility), to extend or decrease conjugation perpendicular to the backbone axis, to alter the electronic properties of the

## Scheme II. PPBP derivatization.



polymer *via* electron withdrawing or donating substituents (e.g. reaction F), to introduce functional sites (e.g. reactions C-E), or to introduce potential ligands (e.g. reaction A) for metal complexation. Polyquinolines can also be derivatized in various ways.

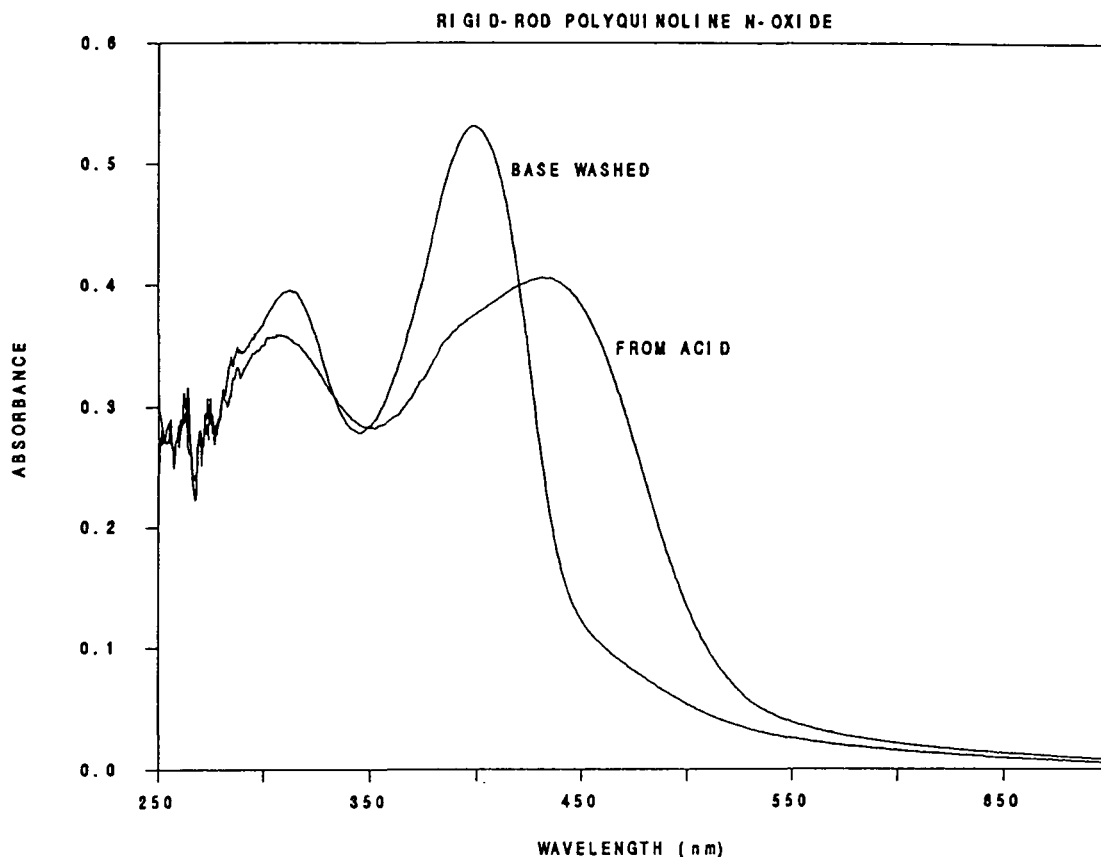
**Polyquinoline N-oxide Derivatives.** We had found that rigid-rod polyquinolines (ROPOQ's) demonstrated similar nonlinear optical properties to our polyparaphenylenes.<sup>17</sup> The ROPOQ's are, however, considerably less processable than Maxdem's polyphenylenes. There have been reports indicating that the solubility of some other nitrogen containing polymers increase upon treatment with hydrogen peroxide, presumably due to the formation of N-oxides. Rigid-rod polyquinolines are typically only soluble in *m*-cresol/diphenylphosphate or concentrated sulfuric acid.<sup>15</sup> However, in the presence of a small amount of 30% hydrogen peroxide, an homogeneous solution up to about 10 percent by weight of ROPOQ could be prepared in trifluoroacetic acid, presumably due to formation of the N-oxide (ROPOQ-NO).

Good quality films of ROPOQ-NO (MAX/JPL-II-300) were cast or spun from solution. The solutions also exhibit shear birefringence, indicative of ordering of the rigid-rod chains. The films typically possess an orange color which fades to yellow upon heating, likely due to loss of residual acid (the protonated rigid-rod PQ's are typically orange). Infrared spectral analysis of either of these films indicates a broad band around 1200 cm<sup>-1</sup>, suggestive of formation of the N-oxide. The absorption (Figure 4) spectrum of the "as cast" film shows two absorption maxima with a valley around 350 nm. The broad absorption extending into the visible sharpens considerably (and tails less into the visible) upon exposure to base, consistent with the observed color change from orange to pale yellow.

**PPBP-Fulvene Derivatives.** By infrared spectroscopy we have observed at least a small fraction of the carbonyl groups in PPBP to undergo a Knoevenagel condensation<sup>32</sup> with sodium cyclopentadienide (NaCp), leading to a fulvene type side chain (Scheme II-A). This derivative is of interest to determine the effect of a highly polarized fulvene group on the inherent nonlinear optical properties of the polymer. In addition, the fulvene functionality also provides a potential site for metal complexation near the conjugated polymer backbone. A tan to light brown film sample (MAX/JPL-II-500) of fulvene-substituted PPBP was submitted\* for testing by JPL. We have also demonstrated that the cyclopentadienide may be conveniently generated *in situ* from dicyclopentadiene and base.

**PPBP-Imine (Schiff Base) Derivatives.** One particularly versatile type of modification which we have pursued involves Schiff base formation (Scheme II-B,C) between amines and the carbonyl groups of PPBP. The imine-forming reaction does not occur as readily as might be expected between aromatic amines and ketones, and we have determined that acid catalysis is generally required for the sterically hindered carbonyl groups present in PPBP. Imine derivatization with aromatic amines should serve to extend conjugation perpendicular to the polymer backbone. The Schiff base derivatives are typically more yellow or orange in color than the unfunctionalized polymers. Elemental analysis indicates that we have been able to achieve about 30-40% conversion of the carbonyl groups to imines. Imine sidechains such as the one derived from methoxyaniline (Scheme II-B) should also possess some dipolar

Figure 4. Absorption spectrum of ROPOQ-NO.



character (withdrawing imine group opposite the donating methoxy group) and could have potential applications in second order nonlinear optical devices.

**PPBP-Oxidized/Reduced Derivatives.** Organic ketones are susceptible to both oxidation and reduction, and we have utilized both modes of reactivity for modification of PPBP. For instance, we have shown that virtually all (as determined by spectrophotometry: Appendix D - Figure 2) of the carbonyl groups of PPBP can be reduced (Scheme II-D) to the corresponding benzhydrol structures by treatment of a solution (phenethyl alcohol) of the polymer with sodium borohydride. The extent of conversion can be readily controlled over a wide range by varying reaction time and/or quantities of reagents. Even though conjugation has been diminished due to loss of the carbonyl group, this derivative is interesting because we have replaced an electron-withdrawing group (-COR) with a modest electron-donating (-CH(OH)Ar) group which might be expected to enhance optical nonlinearity. Oxidation of PPBP (Scheme II-E) appears to be more difficult, but we have achieved moderate conversions (10-35%) by reaction with organic peracids (*m*-chloroperoxybenzoic acid or MCPBA) in methylene chloride. The resulting ester groups can also be hydrolyzed to provide a copolymer with free hydroxy and carboxyl groups. The hydroxy and/or carboxyl groups present in the

oxidized or reduced derivatives are fairly reactive so that many other types of further functionalization are possible.

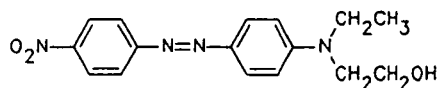
**PPBP-Ketal Derivatives.** The PPBP carbonyl groups can also be derivatized as ketals (Scheme II-F), albeit at lower conversions (20-30%). Again, conjugation (and thus absorption at 355 nm; see Appendix D - Figure 3) is diminished and the sidechain becomes somewhat more electron-donating. Ketal formation provides another potential way to link various types of NLO-active materials to our rigid-rod polymer backbones. A thin film sample (MAX/JPL-II-620) of the ketal derivative was sent to JPL for nonlinear optical characterization.

**Polyparaphenylene blends.** The good solubility of Maxdem's PPP's in common organic solvents like chloroform and NMP suggested that blends with other materials might be readily prepared. For nonlinear optical applications, it is of potential interest to combine the high performance mechanical properties of polyphenylenes with the large optical nonlinearities of less stable polymers or molecular dyes. We have prepared high quality PPBP films by the standard techniques (*vide infra*) which incorporate small amounts (1-5 %) of a wide variety of organic and organometallic dyes (soluble in chloroform or NMP), including:

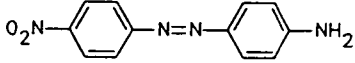
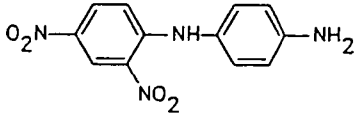
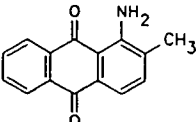
5,10,15,20-Tetrakis(pentafluorophenyl)-21H,23H-porphine  
 tetra(o-hydroxyphenyl)porphine  
 2,3,7,8,12,13,17,18-octaethyl-21H,23H-porphine cobalt(II)  
 5,10,15,20-Tetrakis(4-methoxyphenyl)-21H,23H-porphine cobalt(II)  
 5-nitro-1,10-phenanthroline ferrous perchlorate  
 Sudan Red 7B  
 Sudan Black B  
 Oil Blue A  
 Oil Yellow GRA  
 Oil Red 234  
 Nile Red (fused 4-ring compound)  
 Tetrathiafulvalene  
 Neutral Red  
 Methylene Blue  
 Murexide  
 Vulcan XC 72R carbon black

We have also demonstrated that up to about 30% of certain organic dyes potentially of interest to JPL could be incorporated into films of polyparaphenylenes. We were able to obtain high quality (transparent and visually homogeneous) solution-cast films of PPBP containing the following dyes:

Disperse Red 1



30% wt/wt

Disperse Orange 3		30% wt/wt
Disperse Yellow 9		30% wt/wt
Disperse Orange II		25% wt/wt

Samples (MAX/JPL-II-520, containing 30% dye, and MAX/JPL-II-530, containing 23% dye) of the Disperse Red 1 containing film were submitted for characterization at JPL.

We believe that the ability to prepare such high quality blends stems from the structure of our rigid-rod polyparaphenylenes. The sidechain substituents appended to the rigid-rod backbone likely provide the good processability by preventing efficient packing of the polymers. We believe that this "hairy rod" structure is also responsible for the low density of our polyparaphenylenes because of the relatively large free volumes that presumably arise from the poor packing. We propose that relatively small organics (like the dyes listed above) are able to fit nicely into the free volume within the bulk polymer, allowing good homogeneous blends. Thus, compared to many other high performance polymers which typically possess much higher densities and presumably smaller free volumes, Maxdem's rigid-rod polyparaphenylenes might be uniquely suited for application as a host matrix material for other, more active NLO materials in optical devices.

## Fabrication Techniques

**Solution Casting of Films.** Two methods were utilized for the preparation of good quality solvent cast films of Maxdem's rigid-rod polyparaphenylenes. All films were cast in a particle free and low humidity film chamber which was constructed at Maxdem. We typically filtered polymer solutions through  $\leq 1.2 \mu\text{m}$  filters prior to casting the films. High quality films were achieved with thicknesses ranging from about 0.5 to 3 mils.

(a) In the first method, films were cast from solutions (about 1-15 weight percent, preferably about 3-7 weight percent) in chloroform, anisole, dimethylacetamide (DMAc), N-methylpyrrolidinone (NMP), or other suitable solvents (depending on the solvent volatility desired and on the solubility of the particular polyparaphenylene derivative). Some heating of the more concentrated solutions was occasionally required to prevent gel formation. The solvent was evaporated in the film chamber, if low boiling, or removed in a vacuum or convection oven, if high boiling. The films, especially those thinner than about 1 mil, tended



to be brittle but quite strong. The low humidity environment was critical for casting clear films from solvents like NMP or DMAc, which are relatively nonvolatile and hygroscopic, since moisture causes precipitation of small polymer particles, leading to film cloudiness.

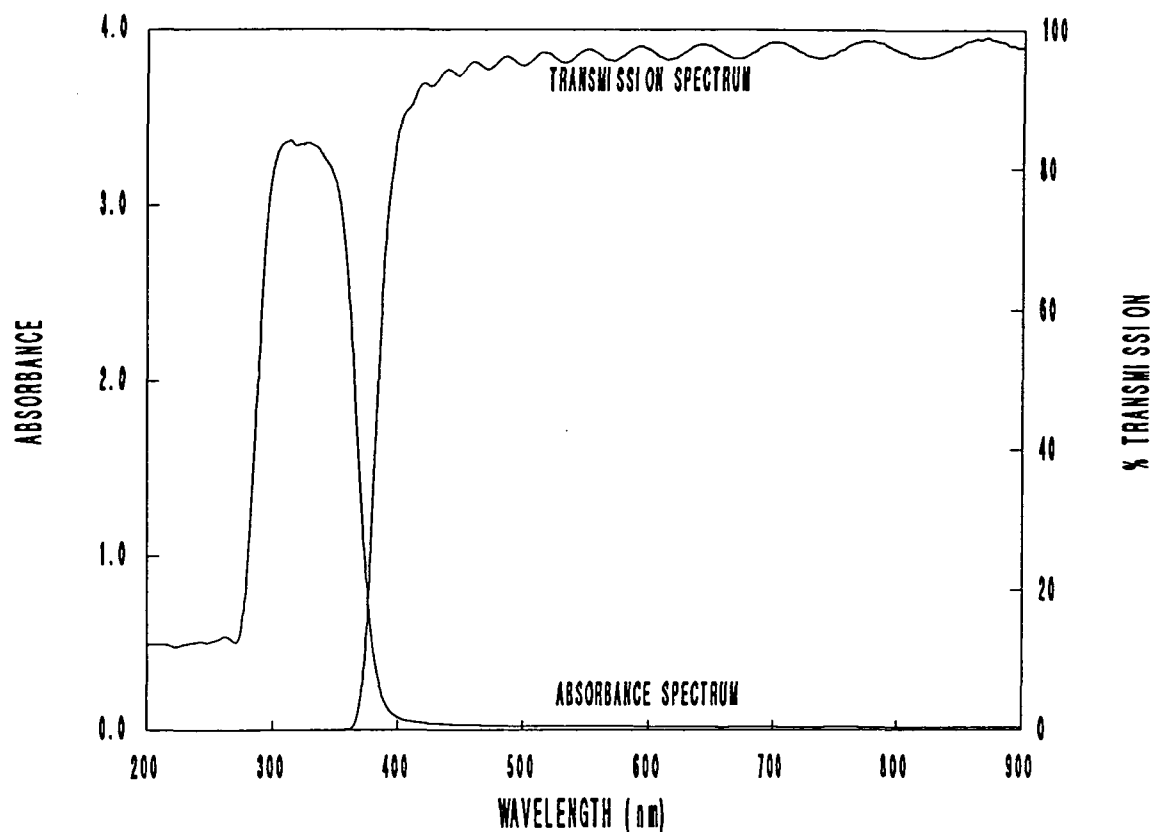
(b) The preferred method for preparing free-standing films of sufficiently soluble polyparaphenylenes involves casting from a solvent mixture of chloroform and NMP (generally containing about 1-10 volume percent NMP, preferably about 1-2 volume percent). Polymer concentrations typically ranged from about 1-15 weight percent, preferably about 3-7 weight percent. After casting the film, the chloroform quickly evaporated, leaving a highly NMP swollen (plasticized) but generally tack-free film. The remaining NMP was removed by heating in an oven to form the final dry film, which tended to be quite optically transparent and colorless. Like those prepared from a single solvent, the completely dried films were brittle but strong. In the "plasticized" state, the films were quite easy to cut without creating cracks that can diminish the measured mechanical properties. The plasticized films can also be stretch oriented, at least to some degree, in order to increase mechanical and, possibly NLO, properties in certain directions.

**Spin-Coating of Thin Films.** Maxdem's rigid-rod polymers are amenable to spin-coating by standard techniques. For example, a thin film sample (MAX/JPL-II-110) of PPBP of roughly 1-2  $\mu\text{m}$  thickness was spun onto a 50 x 45 x 0.19 mm glass slide from NMP solution. The slightly tacky film obtained after the spin coating process was dried overnight in an oven at about 95°C. The resulting film was clear and relatively even, although there were some surface defects noted which were probably due to bubble formation during the oven treatment and/or to the presence of dust (the solutions were filtered prior to casting, but the films were prepared and handled in a typical laboratory environment, not in a clean room). During the Phase I studies, a very thin (0.02  $\mu\text{m}$ ) film of PPP-m was also prepared from NMP solution for optical characterization. Spin-coating has also been performed using other solvents like chloroform (e.g. PPBP and PPPBP) and formic acid (e.g. the ROPOQ N-oxide derivative and dimethylaminobenzoyl-substituted polyparaphenylenes).

The supported thin film of PPBP (MAX/JPL-II-110) demonstrated good light transmission (see Figure 5), except for an interference pattern, above about 400 nm (100% transmission was set using a glass slide vs glass slide; the polymer sample was measured as the supported coating vs a clean glass slide). The absorption spectrum indicates a relatively broad absorption maximum in the range 300-350 nm. This absorption maximum extends to somewhat longer wavelength than that for the polymers prepared during Phase I (PPP-m  $\lambda_{\text{max}} \approx 320 \text{ nm}$ ), perhaps indicative of increased conjugation.

**Thermoforming.** Maxdem's rigid-rod polyparaphenylenes can be compression molded at relatively moderate temperatures (200-350°C) and pressures (200-2,500 psi). Samples of PPBP undergo some darkening upon molding at these temperatures, but the mechanical properties do not seem to be affected. Although the darkening is likely due to some small amount of decomposition, the more highly colored panels often seem to show somewhat better properties (better chemical resistance and better tensile and flexural properties). We believe that the decomposition is largely due to residual impurities since the darkening seems to

**Figure 5.** Absorption and transmission spectra of spun PPBP film (MAX/JPL-II-110).



become less severe as higher polymer purities are achieved. In other work, we have discovered that certain of Maxdem's polyparaphenylenes can even be injection molded (e.g. PPPBP can be injection molded at 280°C using a pressure of 2,000 psi). Unfortunately, we have not yet been able to form optical quality parts by compression or injection molding.

## Characterization of Rigid-Rod Polymers

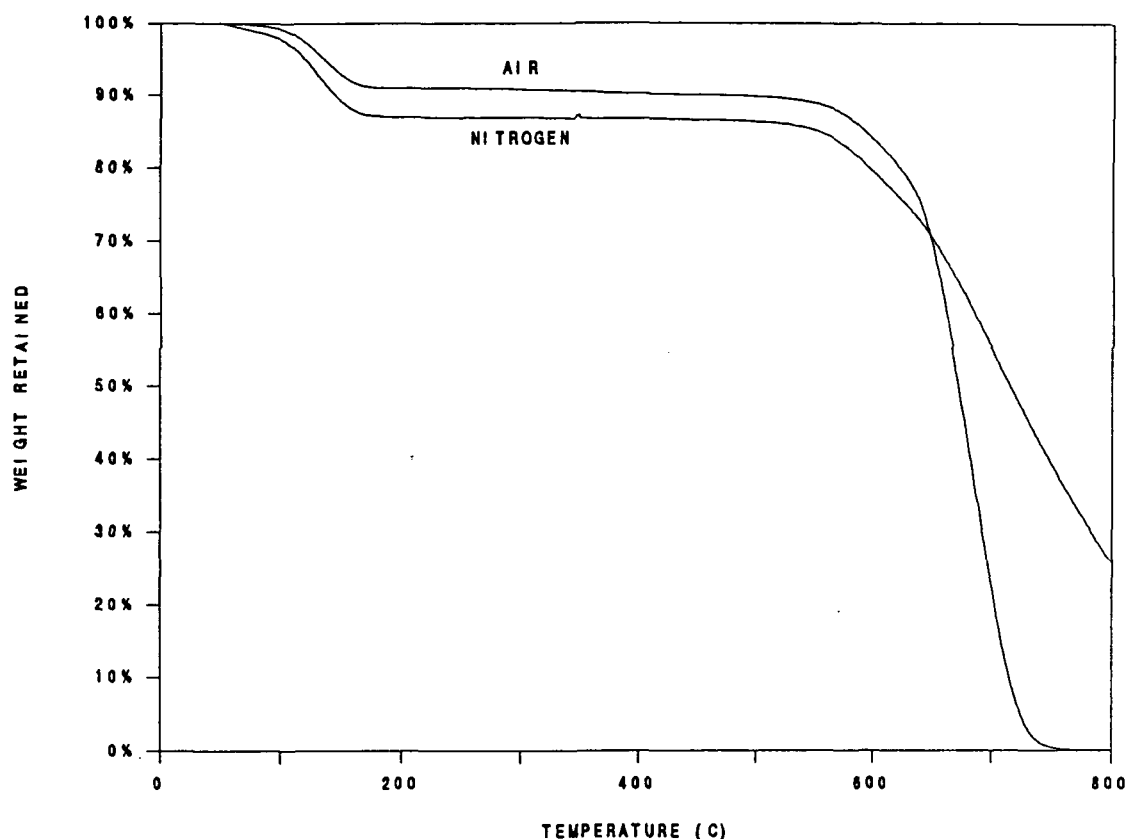
The properties of Maxdem's rigid-rod polymers are discussed below. Additionally, the properties of some of Maxdem's rigid-rod polyparaphenylenes (PPBP and PPPBP) are summarized in the data sheets in Appendices B and C.

**Properties of Rigid-Rod and Ladder Polyquinolines.** The chemical, physical, mechanical, and electrical properties of polyquinolines, including rigid-rod derivatives, have largely been reviewed by Stille.<sup>15</sup> In general, rigid-rod polyquinolines demonstrate remarkable thermal and thermooxidative stability, very high glass transition temperatures (typically 300-400°C), excellent electrical properties (low dielectric constants and loss tangents and high dielectric strength), and high mechanical strength and stiffness. The major drawbacks with rigid-rod polyquinolines are their relatively poor processability (only from strongly acidic solvents) and relatively high cost. The rigid ladder type structures that we attempted to

prepare during the Phase II work were essentially intractable and essentially no further characterization was performed. The synthesis, characterization, electro-optical properties, and problems of various types of ladder polymers has recently been reviewed.<sup>33</sup>

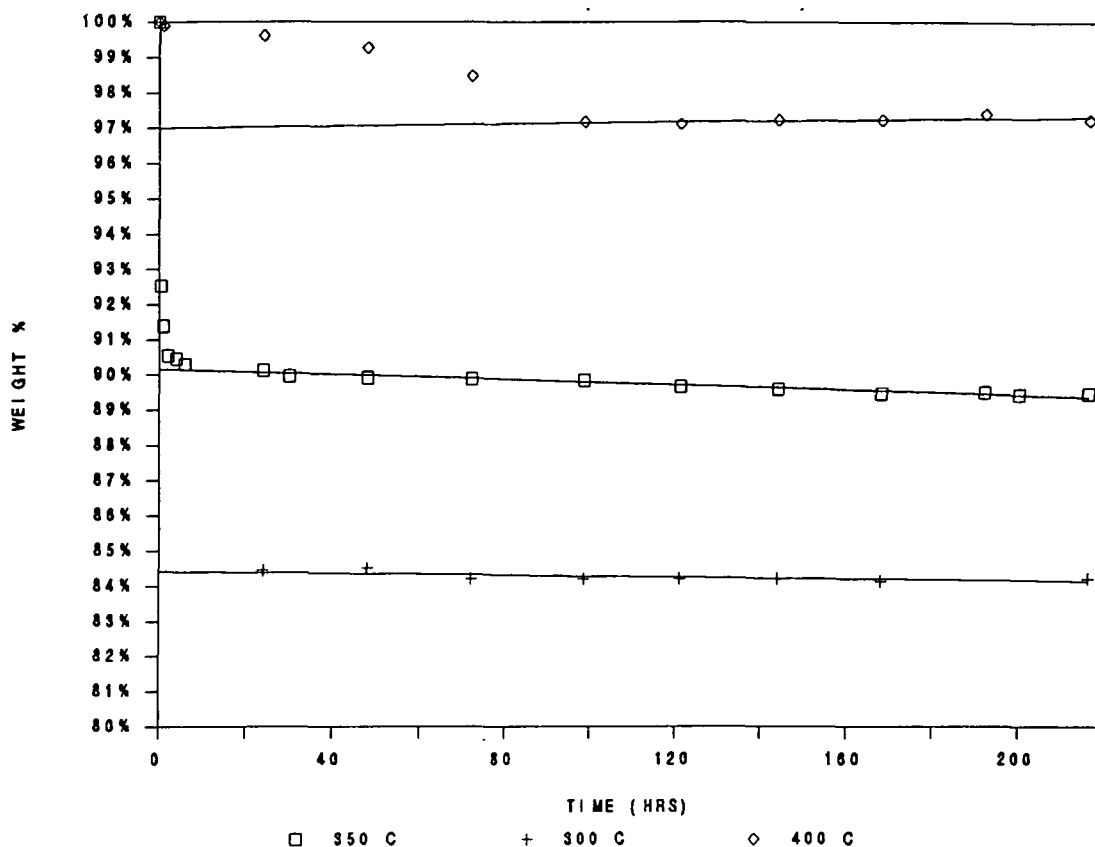
**Thermal Properties.** Thermogravimetric analysis (TGA) indicated that Maxdem's polyparaphenylenes demonstrated excellent thermal stability. For instance, PPBP does not exhibit significant decomposition below 500-600°C as shown in Figure 6 (the weight loss observed below 200°C is due to residual solvent, NMP, in the sample).

**Figure 6.** Thermogravimetric analysis of PPBP (10°C/min).



Such experiments, however, are of relatively short duration and do not always accurately reflect the thermal stability of a materials under actual use conditions. A somewhat more rigorous test of thermal stability involves monitoring weight loss of a material over an extended period of time at some temperature (isothermal weight loss). Film samples of PPBP were examined at temperatures of 300, 350, and 400°C in air for over 200 hours and demonstrated excellent weight retention (Figure 7). The rapid initial weight loss is almost certainly due to residual solvent (NMP) in the films.<sup>34</sup> After such treatment, the films darken somewhat in color, become stiffer (possibly due to complete loss of residual solvent and/or some degradative crosslinking), and become insoluble. We have not measured the mechanical properties after thermal aging.

Figure 7. PPBP isothermal weight loss (the initial weight loss is due to residual solvent).



Although the rigid-rod polyparaphenylenes demonstrate high thermal stability, they possess surprisingly low glass transition temperatures ( $T_g$ 's) for high performance aromatic polymers. The low  $T_g$ 's, typically between 130-200°C depending on the derivative and its molecular weight, likely contribute to the desirable processing characteristics of the materials but may limit the use of these materials for high temperature applications (a polymers maximum use temperature is determined from a consideration of its thermal stability and mechanical properties, which decrease above  $T_g$ , at that temperature). Fortunately, we have observed, during other studies, that the  $T_g$  often increases at least somewhat after certain types of thermal processing, possibly due to a small amount of thermally induced crosslinking (possibly promoted by some residual impurities).

The value of a materials coefficient of thermal expansion (CTE) is critical for many types of applications, including electro-optical applications, and the CTE's of rigid polymers is expected to be desirably low. Measurements of CTE (by TMA analyses) for Maxdem's polyparaphenylenes are still preliminary but do typically indicate the low values expected for rigid-rod polymers. For instance, isotropic samples (e.g. compression molded) of PPBP and

PPBP typically demonstrate linear CTE's of about 30-40 and 60-70 ppm/°C, respectively. If processing techniques are utilized that lead to better consolidation (less residual stress) and/or some degree of orientation (e.g. injection molding or film casting from solution), then values as low as 5 ppm/°C (and typically between 5-25 ppm/°C) have been measured. The ability to vary CTE's of the rigid-rod polymers to match different substrates (thus reducing thermal stresses) that might be utilized in electro-optic devices could be an important advantage of these materials.

**Chemical Properties of Maxdem's Polyphenylenes.** Compared to other "processable" rigid-rod polymers (namely polybenzazoles and polyquinolines), Maxdem's substituted polyparaphenylenes demonstrate excellent solubility characteristics in a wide variety of *common organic solvents*. Thus, depending on the specific derivative, solubility has been observed in solvents ranging from methylene chloride, chloroform, chlorobenzene, o-dichlorobenzene, anisole, m-cresol, aniline, diphenyl ether, NMP, DMAc, formic acid, sulfuric acid, hexafluoroisopropanol (HFIP), and tetrahydrofuran (THF). Good chemical resistance is observed, however, for other types of solvents including aliphatic and aromatic hydrocarbons, aliphatic alcohols, water, and strong bases. In addition, samples which have been thermally molded, often demonstrate greatly decreased solubility and increased chemical resistance, possibly due to a relatively small amount of thermally induced crosslinking or crystallization.

**Physical and Mechanical Properties of PPBP and PPPBP.** Fairly extensive physical and mechanical testing has been performed on thin film and compression molded samples of PPBP and to a more limited extent of PPPBP as summarized in Appendix 1. The results have been measured at several different laboratories and using different batches of these developmental polymers, accounting for the fairly large ranges of reported values. In general, these polymers demonstrate isotropic strengths (typically  $\geq 20,000$  psi) and stiffnesses (typically  $\geq 1.0$  msi) that cannot be attained with other polymers without using reinforcing fibers or fillers. In fact, the properties of PPBP and PPPBP most closely resemble those of common chopped fiber composites, but without the deleterious effects caused by the presence of the fibers (e.g. higher density, poorer electrical properties and moisture absorption, fiber/matrix interfacial stresses, reduced optical properties, etc.).

**Electrical Properties of PPBP and PPPBP.** Materials used for optical and hybrid electro-optical devices will have to meet many of the same stringent requirements as materials currently used in the microelectronics industry. Although there are many required properties that a successful material must possess, of prime importance are dielectric properties and moisture absorption. Polymers are typically utilized as insulating dielectric layers and coatings, thus low dielectric constants and low loss tangents are extremely important. The polyparaphenylenes studied herein demonstrate desirable values for these properties - better than or at least competitive with many polymers (especially polyimides) currently utilized in the microelectronics industry but possibly somewhat poorer than some of the state-of-the-art materials (e.g. certain flexible polyquinolines<sup>35</sup>) being developed for ultra-high performance electronic devices. Moisture absorption is also very important because the dielectric properties of a polymer often change drastically according to the amount of absorbed moisture. Fortunately, both polyquinolines and polyparaphenylenes have demonstrated extremely low

tendencies to absorb moisture (less than 0.25 wt % at 75°C and 75% relative humidity after 24 hours).

**Optical Properties of Rigid-Rod Polyparaphenylene Derivatives.** A simple figure of merit for the effective third order optical nonlinearity of a material is the quantity  $\chi^{(3)}/\alpha$ , where  $\alpha$  is the absorption coefficient at the third harmonic. Thus, for some applications, the practical benefit of a material with a very high value of  $\chi^{(3)}$  can be diminished if the material absorbs too much of the new light frequency that is generated. While trying to extend conjugation in our rigid-rod polymers to increase the optical nonlinearity, we have also likely shifted the UV absorption maximum further out into the visible, thus increasing the absorption coefficient ( $\alpha$ ).

We have measured the values of  $\alpha$  for several of the new derivatives that have been prepared during this Phase II work. Some of them have been found to be significantly higher than the  $1.8 \mu\text{m}^{-1}$  ( $1,800 \text{ mm}^{-1}$ ) found for PPP-m. Therefore, we have also performed PPBP modifications (Scheme II-D, II-E) which reduce the overall conjugation but offer lower absorption. The measurement for PPP-m was performed by spin-coating a thin film, measuring the absorbance, and measuring the thickness with a profilometer (Phase I work). The coefficients for newer derivatives were calculated by measuring the absorbance of solutions (in NMP) and deriving the absorbance for the pure material from the known solution concentration and estimated film density (about  $1.2 \text{ g/cm}^3$ ):

<u>Derivative</u>	<u><math>\lambda_{\text{max}}</math></u>	<u><math>\alpha \text{ (mm}^{-1} \text{ @ 355 nm)}</math></u>	<u>Method</u>
PPBP	330 nm	3,600	solution
PPP-m	320 nm	1,800	thin film
phenyl	324 nm	580	solution
PPBP-benzhydrol	318 nm	250	solution

We expect that PPPBP, and other substituted benzoylphenylene structures, should have similar  $\alpha$  to PPBP, although quantitative measurements have not been performed. Considering the high conversion possible with the reduction reaction to yield the benzhydrol derivative, we suspect that this derivative could be representative of a rigid-rod polyparaphenylene with about the smallest  $\alpha$  value possible. However, we have not yet made measurements to determine what effect the incorporation of 1,3-phenylene linkages (leading to kinked structures with relatively short lengths of *para*-linked segments) will have on the absorption behavior of these polymers. We also have not quantified  $\alpha$  values for copolymers containing unsubstituted *para*-phenylene units.

## ESTIMATES OF TECHNICAL FEASIBILITY

This Phase II Contract was primarily directed toward tailoring the chemical structure of Maxdem's rigid-rod polyparaphenylenes and polyquinolines, or otherwise modifying them, to maximize nonlinear optical (NLO) properties, especially third order susceptibilities, while retaining desirable processing and mechanical properties. Many rigid-rod derivatives were synthesized and fabricated into samples (free-standing or supported films or molded specimens) for various types of mechanical, electrical, and optical testing. We have submitted several samples to JPL for evaluation of NLO properties (see Appendix A), but no results have been reported to us. The promise of Maxdem's rigid-rod polymers for electro-optic applications needs to be evaluated at several different levels: general materials synthesis and properties, inherent third order NLO properties and applications, and second order NLO properties and applications.

### Materials Synthesis and Properties

**Polyquinolines.** The synthesis of rigid-rod polyquinolines (ROPOQ) is relatively straightforward, although the monomers are somewhat elaborate and thus expensive. We have attempted to extend this synthesis to various formulations of polyquinoline ladder polymers but were largely unsuccessful due to the intractable nature of these highly conjugated materials. Such materials are expected to demonstrate good NLO susceptibilities and electrical conductivity<sup>33</sup> but are not practical if they cannot be fabricated into useful forms. Several model ladder fragments were sent to JPL for nonlinear optical testing (not yet performed). If any such fragments were to demonstrate desirable NLO properties, they could potentially be utilized in copolymeric systems, wherein NLO properties are contributed by the polyquinoline segments and processability is achieved by proper choice of the co-segments. Related types of complementary copolymers have been examined by other workers.<sup>31</sup>

Polyquinolines possess outstanding thermal, mechanical, and electrical properties and offer many advantages for specialty, high-value-added microelectronic and electro-optic applications where ultra-high performance is absolutely necessary.<sup>35</sup> The ROPOQ's, however, are also somewhat difficult to process (strong acid solvents only) and are expensive. We have been able to increase the processability considerably by formation of the N-oxide derivative of ROPOQ (ROPOQ-NO). Thus, the solubility was greatly increased in trifluoroacetic acid (still acidic but easier to handle than the acids required for unmodified ROPOQ), from which good quality films can be readily prepared by casting or spin-coating. Less rigid polyquinolines (e.g. Maxdem's PQ-100™) do exhibit much better processability from common organic solvents (e.g. toluene and NMP) but were not examined for NLO applications during this project since they do not have highly extended conjugated backbones considered necessary for high  $\chi^{(3)}$  values. Such polymers could, however, potentially serve as host matrices for NLO active moieties in NLO devices or as simple dielectric layers in hybrid electro-optical devices.

**Polyparaphenylenes.** The polymerization of variously substituted dichlorobenzophenone monomers to high molecular weight polyparaphenylenes has been reproducibly achieved (for this contract as well as for various other projects) at scales of up to 1 kg / batch; further scaleup is expected to be relatively straightforward. Molecular weight control is also possible and polymers with intrinsic viscosities from about 0.5-8 dL/g have been obtained. Maxdem's polyparaphenylenes actually represent a new class of polymers, with many different derivatives being possible by varying the identity and/or orientation of the substituent groups. The different substituents affect the chemical, mechanical, and electronic properties of the polymer in predictable ways and, in some cases, can be utilized for further functionalization. Several other derivatives have been prepared *via* Maxdem's polymerization route at smaller scales including polypara-(phenylphenylene), polypara-(benzoylmorpholine), polypara-(benzoylpiperidine), and various types of copolymers. Maxdem's polyparaphenylenes will be inexpensive relative to polyquinolines, and they should be amenable to scaleup to commodity levels while still providing the chemical flexibility (as demonstrated by the many different derivatives prepared during this contract) necessary to provide custom derivatives to address specific high-value-added applications (e.g. electro-optics).

Even though our polyparaphenylenes demonstrate moderate third order nonlinear optical effects ( $\chi^{(3)} \approx 10^{-12}$ ), it has been their processability and chemical and mechanical properties that has most warranted further attention. Other materials have been identified with greater optical nonlinearities ( $\chi^{(3)}$ ), but they typically possess poor mechanical properties and many are intractable. Maxdem's rigid-rod polyparaphenylenes can be processed from *common organic solvents* and can even be thermally molded to give parts with excellent mechanical (strength and stiffness) and thermal (stability and low thermal expansion) properties. Maxdem's rigid-rod polymers also possess very desirable optical (good transparency in the visible spectrum) and electronic properties (low dielectric constant and moisture absorption). No other polymer system demonstrates the unique combination of properties of our processable polyparaphenylenes; a combination of properties that also fits the needs of many projected electro-optical applications.

## Third Order NLO Properties and Applications

We have synthesized specific derivatives, employing the following methodologies, in order to try to optimize the third order nonlinear optical susceptibilities of our rigid-rod polyparaphenylenes:

(1) **Increasing conjugation perpendicular to the polymer backbone.** The carbonyl linked sidechains in the polypara-(benzoyl-phenylene) derivatives and the pendant phenyl group in PPPP serve to increase conjugation perpendicular to the polymer backbone. Although one-dimensional electron delocalization seems to be critical for good nonlinearities, we expect that extended two-dimensional delocalization could also increase the values of  $\chi^{(3)}$ . Unfortunately, however, the increased conjugation typically increases the absorption coefficient and shifts the absorption maximum more toward the visible. Thus, the effects of added



conjugation on the more practical figure-of-merit,  $\chi^{(3)}/\alpha$ , may be somewhat mitigated due to the concomitant increase in  $\alpha$ .

**(2) Polyparaphenylene copolymers containing unsubstituted phenylene units.**

Presumably these copolymers will have increased conjugation along the polymer backbone due to a decrease in the number of substituent groups that cause twisting of adjacent phenylene rings. We carried out copolymerizations involving one of our more soluble Type I monomers, 2,5-dichloro-4'-phenoxybenzophenone, but the copolymer solubility has not been as promising as expected, possibly due to the presence of large blocks of unsubstituted polyparaphenylene. Other copolymers incorporating comonomers with longer sidechains may be necessary to make such types of copolymers more processable. We have also prepared copolymers containing a combination of unsubstituted 1,3-phenylene and 1,4-phenylene linkages which yield somewhat more soluble copolymers, but the *m*-phenylene linkages (kinks) will disrupt conjugation between rigid segments.

**(3) Derivatization to alter NLO properties.** We have demonstrated that PPBP can be readily modified via chemical functionalization (e.g. Scheme II). The carbonyl group of PPBP has been shown to undergo many of the chemical transformations common to normal organic ketones: e.g. imine formation, ketal formation, oxidation, and reduction. We have utilized this reactivity to prepare derivatives that can be utilized to determine the relative importance of parameters such as extended conjugation, position of absorption maximum, value of the absorption coefficient ( $\alpha$ ), and electron density in the conjugated system.

The current consensus within the scientific community suggests that third order nonlinear optical applications of organic and polymeric materials is still far in the future due to the lack of basic understanding of the third order processes.<sup>4</sup> While we hope that the derivatives prepared during this contract will further the body of information that will eventually lead to sound structure-property relationships between chemical structure and optical nonlinearity, we have not identified a specific third order NLO material, based on polyquinolines or polyparaphenylenes, or device application that is well suited for further development during Phase III at this time. More research work is primarily required in order to fully identify the important parameters for practical third order applications.

## Second Order NLO Applications

While this contract was primarily centered on third order NLO properties and applications of Maxdem's rigid-rod polymers, we realized during the course of the work that second order NLO applications were much closer to practical realization. We therefore, performed some preliminary work aimed at identifying promising second order properties and applications of our rigid-rod polymers. In particular, we performed some initial studies aimed at characterizing the potential inherent second order nonlinearity ( $\chi^{(2)}$ ) of certain of our derivatives with the proper structures and in identifying the possibility of preparing composite second order materials utilizing our polymers with other highly nonlinear optical compounds.

**Inherent Second Order NLO Properties.** Certain of the polyparaphenylene derivatives that we prepared possess geometries leading to a somewhat dipolar sidechain (e.g. withdrawing carbonyl groups opposite donating groups like -OR or -NR<sub>2</sub>). Thin films of such derivatives could be employed for devices based on second order NLO by poling to induce orientation of the dipoles above T<sub>g</sub>. The nonlinearities are expected to be small for these types of compounds since much more elaborate compounds, designed to maximize delocalization over extended lengths, are typically required to achieve large nonlinear effects.<sup>36</sup> In a practical sense, however, readily processable materials with moderate NLO properties, but good mechanical properties, may find applications sooner, and of a wider scope, than the more elaborate materials mentioned above. In particular, one of the current problems with second order devices based on organic polymers is poor stability - relaxation of the oriented dipoles achieved by poling - which ultimately leads to loss of the nonlinearity over time. Researchers at JPL are currently trying to pole thin films of two different polyparaphenylene derivatives and measuring any resulting second order effects. If alignment can be induced within these rigid-rod polymers, which possess very high modulus and viscosity compared to typical polymers, above T<sub>g</sub>, it is expected that it would be strongly locked in below T<sub>g</sub>, leading to excellent device stability.

**Composite Second Order NLO Materials.** A second approach for achieving second order NLO materials involves blending compounds (e.g. usually conjugated dipolar organic molecules or dyes) possessing high  $\chi^{(2)}$ 's with Maxdem's rigid-rod polymers. The rigid-rod polymers serve as high performance host matrices which provide the required mechanical and thermal properties required for practical devices. During Phase II work, we demonstrated that significant amounts, up to 30% by weight, of several types of dye molecules could be incorporated into high quality films of the polyparaphenylenes. The rigid-rods provide advantages over other types of polymer hosts because of their good processability (solubility in solvents that dissolve the dyes) and mechanical properties. We also think that the special structure of our polyparaphenylenes yields large free volumes within the consolidated polymer which enables the incorporation of large quantities of dyes. We also expect device stability to be good because of the high viscosity and modulus of the rigid-rod polymers, which should cause diffusion (relaxation) of the aligned dipolar dyes to be greatly slowed.

## Summary

Aside from having good linear and nonlinear optical properties, candidate polymers for optical devices will have to meet stringent requirements similar to those faced by materials for electronics applications. Indeed, most nonlinear optical devices will likely be hybrids between optical and electronic devices. In other work, Maxdem has shown that certain polyquinolines possess especially promising properties for microelectronic applications.<sup>35</sup> During this work, we have measured the relevant properties of PPBP and PPPBP free-standing thin films, and these look promising as well. The rigid nature of these polymers confers good mechanical strength and low coefficients of thermal expansion. Their relatively nonpolar structure are likely responsible for the low moisture absorption and dielectric constants. We have also previously

demonstrated that polyparaphenylenes possess good thermal and thermooxidative stability and good optical transparency throughout the visible spectrum. Maxdem's rigid-rod polyparaphenylenes exhibit a unique combination of chemical, mechanical, electrical, and optical properties that is unmatched by any other organic polymer system. In addition, our processable polyparaphenylenes comprise an entire family of derivatives so that many different structures are available to specifically address the needs of different applications. For electro-optical as well as many other applications (e.g. structural), Maxdem will be continuing the development of our rigid-rod polymers.

Currently, in light of the work performed during this contract and that performed by others in the field, we think that commercial third order NLO applications are still considerably distant and, therefore, will not be immediately pursued in a Phase III effort. Much more basic scientific information needs to be obtained before third order NLO processes in organic polymers are sufficiently understood for practical device applications. We anticipate that the work performed during this contract and any measurements performed by JPL at a later time will help to advance third order NLO science and technology. In contrast, second order NLO applications are much nearer to commercial realization, and Maxdem's polymers may prove useful as new nonlinear optical polymers or, perhaps more probably, as high performance polymeric hosts for other nonlinear optical compounds.

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20. The majority of this synthesis work was not directly supported by the Phase II contract, nor was a significant amount of the resulting material utilized for nonlinear optical studies. We merely wish to demonstrate the progress of the general technology. Note that for a given degree of polymerization (chain length), PPPBP is expected to have a lower intrinsic viscosity than PPBP because of its longer sidechain.
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## APPENDIX A

### List of Samples

#### Second Quarter:

MAX/JPL-II-110	Spin-coated PPBP film (1-2 $\mu\text{m}$ ) from NMP
MAX/JPL-II-120	Free-standing PPBP film (1-3 mil) from $\text{CHCl}_3$
MAX/JPL-II-200	3-Ring Polyquinoline ladder fragment - solution
MAX/JPL-II-210	5-Ring Polyquinoline ladder fragment - solution
MAX/JPL-II-220	5-Ring Polyquinoline ladder fragment - solution
MAX/JPL-II-300	ROPOQ N-oxide thin film

#### Third Quarter:

MAX/JPL-II-400	Free-standing PPPBP thin film
MAX/JPL-II-410	80/20 PPPBP/p-dichlorobenzene copolymer
MAX/JPL-II-420	50/50 PPPBP/p-dichlorobenzene copolymer
MAX/JPL-II-430	80/20 PPPBP/p-dibromobiphenyl copolymer
MAX/JPL-II-440	50/50 PPPBP/p-dibromobiphenyl copolymer
MAX/JPL-II-450	80/20 PPPBP/p-dibromonaphthalene copolymer
MAX/JPL-II-460	50/50 PPPBP/p-dibromonaphthalene copolymer

#### Fifth Quarter:

MAX/JPL-II-500	PPBP-fulvene derivative - thin film sample
MAX/JPL-II-510	PPBP-imine derivative - thin film sample
MAX/JPL-II-520	30% Disperse Red I/PPBP blend - thin film sample
MAX/JPL-II-530	23% Disperse Red I/PPBP blend - thin film sample

#### Sixth Quarter:

MAX/JPL-II-600	Polypara-4'-(N,N-dimethylaminobenzoyl)phenylene film
MAX/JPL-II-610	PPBP-benzhydrol derivative - thin film sample
MAX/JPL-II-620	PPBP-ketal derivative - thin film sample

#### Seventh Quarter:

MAX/JPL-II-700	85/15 PPBP/ <i>m</i> -DCB Copolymer Film
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#### Eighth Quarter:

MAX/JPL-II-800	Polypara-4'-( $\text{Me}_2\text{N}$ -benzoyl)phenylene resin
MAX/JPL-II-810	85/15 Polypara-4'-( $\text{Me}_2\text{N}$ -benzoyl)phenylene/ <i>m</i> -DCB
MAX/JPL-II-820	PPPBP resin

## APPENDIX B

### Polyparaphenylene Properties - PPBP

Intrinsic Viscosity (0.05 M LiBr/NMP at 40°C)	5.0-7.0 dL/g
Density	1.21
Thermal Properties	
Glass Transition Temperature, $T_g$ (DSC)	140-160°C
Glass Transition Temperature, $T_g$ (DMTA)	162-172°C
Linear CTE below $T_g$ (cast films; TMA)	5-25 ppm/°C
Linear CTE below $T_g$ (molded parts; TMA)	30-40 ppm/°C
Thermal Stability	
5% Wt Loss Temperature/Air (TGA)	526-583°C
5% Wt Loss Temperature/ $N_2$ (TGA)	530-575°C
Tensile Properties (ASTM-D-882; thin films)	
Tensile Strength	20-35 KSI
Tensile Modulus	1.5-2.6 MSI
Elongation to break	1.0-2.0 %
Flexural Properties (ASTM-D-790; molded specimens)	
Flexural Strength	20-45 KSI
Flexural Modulus	1.0-1.5 MSI
Electrical Properties (thin films)	
Dielectric Constant	
IPC-TM-650 @ 1 MHz	3.3
ASTM-D-150 @ 1 KHz	3.4
ASTM-D-150 @ 60 Hz	3.4
Dielectric Loss	
IPC-TM-650 @ 1 MHz	0.005
ASTM-D-150 @ 1 KHz	0.014
ASTM-D-150 @ 60 Hz	0.014
Dielectric Strength (kV/mil @ 1 mil)	1.7 ± 1.2
Moisture Uptake (24 hrs / 75°C / 75% RH)	0.25 %
Hardness - Shore D	95
Hardness - Barcol	75
Solubility	NMP, DMAc, <i>m</i> -cresol, anisole, $CH_2Cl_2$
Melt Processibility (molding conditions)	compression



## APPENDIX C

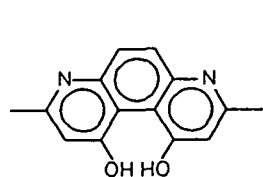
### Polyparaphenylene Properties - PPPBP

Intrinsic Viscosity (0.05M LiBr/NMP at 40°C)	3.5-5.0 dL/g
Density	1.23
Thermal Properties	
Glass Transition Temperature, $T_g$ (DSC)	140-155°C
Glass Transition Temperature, $T_g$ (DMTA)	149-178°C
Linear CTE below $T_g$ (cast films; TMA)	15 ppm/°C
Linear CTE below $T_g$ (molded parts; TMA)	60-70 ppm/°C
Thermal Stability	
5% Wt Loss Temperature/Air (TGA)	490-505°C
5% Wt Loss Temperature/ $N_2$ (TGA)	505-515°C
Tensile Properties (ASTM-D-882; thin films)	
Tensile Strength	15-30 KSI
Tensile Modulus	0.9-1.5 MSI
Elongation to break	1.0-2.0 %
Flexural Properties (ASTM-D-790; molded specimens)	
Flexural Strength	15 KSI
Flexural Modulus	0.7-1.1 MSI
Electrical Properties (thin films)	
Dielectric Constant	
IPC-TM-650 @ 1 MHz	3.0
ASTM-D-150 @ 1 KHz	3.2
ASTM-D-150 @ 60 Hz	3.2
Dielectric Loss	
IPC-TM-650 @ 1 MHz	0.002
ASTM-D-150 @ 1 KHz	0.0023
ASTM-D-150 @ 60 Hz	0.0030
Dielectric Strength (kV/mil @ 1 mil)	2.3 ± 1.2
Moisture Uptake (24 hrs / 75°C / 75% RH)	-----
Hardness - Shore D	93
Hardness - Barcol	-----
Solubility	NMP, DMAc, <i>m</i> -cresol, anisole, $CH_2Cl_2$
Melt Processability (molding conditions)	compression / injection

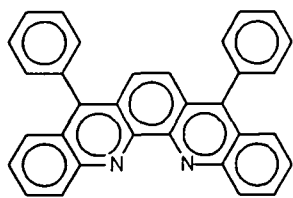
## APPENDIX D

### ABSORPTION SPECTRA

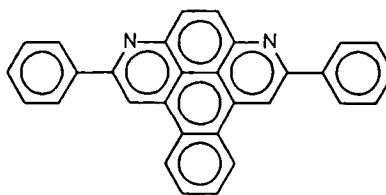
Figure 1. Absorption spectra of polyquinoline ladder fragments.



MAX/JPL-II-200



MAX/JPL-II-210



MAX/JPL-II-220

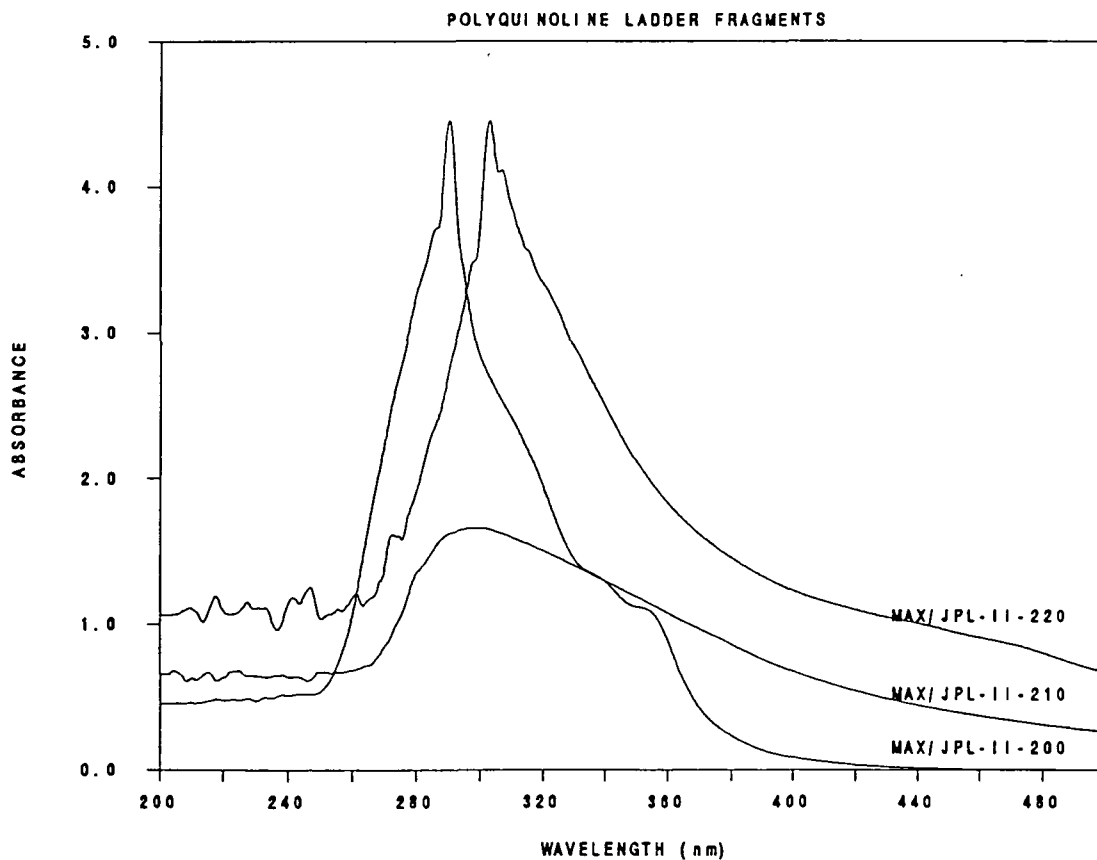


Figure 2. Absorption spectrum of PPBP and its benzhydryl derivative (NMP solution).

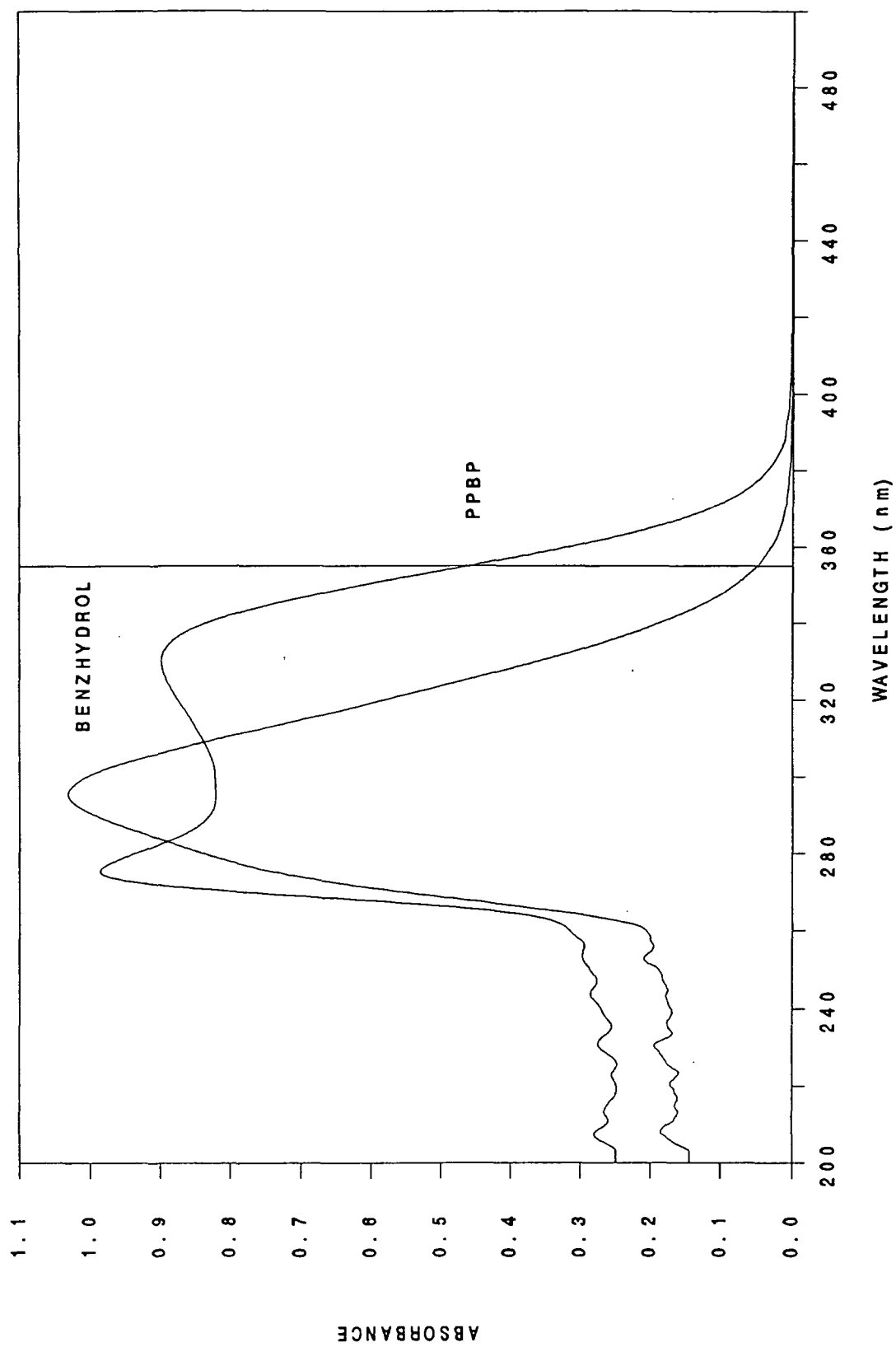
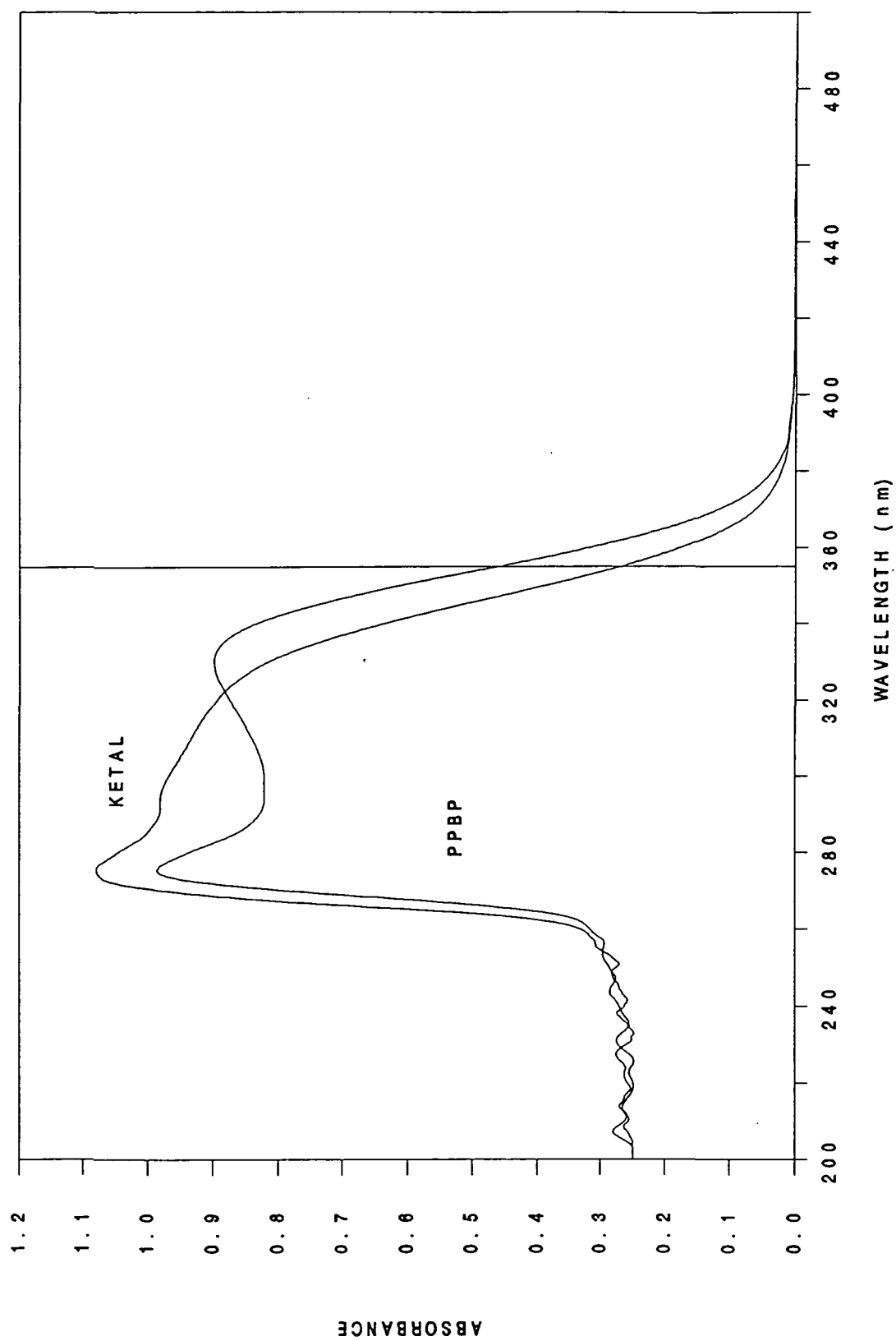


Figure 3. Absorption spectrum of PPBP and its ketal derivative (NMP solution).



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16. Abstract  Several routes have been explored for the modification of Maxdem's novel conjugated rigid-rod polymers in order to optimize their nonlinear optical (NLO) properties while retaining their desirable processing and mechanical properties. Several derivatives have been prepared and high quality film samples have been prepared for optical testing. As a class, the materials possess high mechanical strength (tensile strength $\approx$ 10-40 KSI) and stiffness (tensile modulus $\approx$ 1-3 MSI), good thermal and thermooxidative stability, low moisture uptake ( $<0.5\%$ ), low thermal expansion (5-70 ppm/ $^{\circ}$ C), and low dielectric constants (3.0-3.3) - properties which will be important for electro-optic device fabrication. All of the rigid-rod polymers studied can be processed by solution techniques (film casting and spin-coating), and some of the more processible derivatives can be thermally molded. The polymers also demonstrate good optical transparency with low absorption coefficients ranging from about 250-3,600 $\text{mm}^{-1}$ at 355 nm for thin films. Several of the derivatives look promising as dielectric materials for microelectronic or opto-electronic applications and others appear potentially promising as second order NLO polymers or as high performance host matrices for NLO dyes. Third order NLO applications still seem to be far from commercial realization.					
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